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INTERFACIAL STUDIES OF WHISKER AND COATED FIBER REINFORCED CERAMIC MATRIX COMPOSITES

Prepared by

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The objectives of this program are to characterize the interfacial region in a variety of whisker and coated fiber reinforced glass-ceramic matrix composites, and to study how the structure, chemistry, and bonding characteristics of the interface influence composite properties such as strength, toughness, and environmental and thermal stability.

During the past year, efforts in the whisker composite area were focused on the investigation of whisker coatings such as carbon and BN on LAS glass-ceramic matrix composite properties, fabrication and characterization of calcium aluminosicicate (CAS) matrix/SiC whisker composites, high resolution TEM studies of a variety of SiC whisker/LAS matrix composite interfaces, characterization of composite fracture toughness by a variety of techniques, and the evaluation of SiC platelets as an alternate reinforcement to whiskers. Efforts in the coated fiber area were focused on the evaluation of yttria and BN coated NICALON fibers from General Atomics. Results of these studies are presented. Key ...

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I. INTRODUCTION

During the past decade, the interest in ceramic matrix composites for high temperature structural applications, especially for use in heat engines, has increased to the point that a large number of industrial organizations as well as universities and government laboratories throughout the world are actively performing research into a myriad of different systems and different processing procedures for these materials. Among the types of ceramic matrix composites under investigation are whisker reinforced glasses and glass-ceramics[1-4] as well as whisker reinforced crystalline ceramics[5-34], and continuous fiber reinforced ceramics produced by methods that include hot-pressing of glasses and glass-ceramics[35-50], sol-gel infiltration and pyrolysis of ceramics[51], polymer precursor infiltration and pyrolysis[52], reactive oxidation of metals[53], reactive sintering[54], and chemical vapor infiltration (CVI) of silicon based ceramics[55-66].

It has been found in all of the above-mentioned ceramic composites that in order to achieve high strength and, in particular, high toughness, the bonding at the fiber/matrix interface must be controlled such that bonding is strong enough to allow load transfer from the matrix to the fibers under stress but weak enough so that an advancing matrix crack can be deflected by the fibers. In addition, the nature of the fiber/matrix interface must include resistance to oxidation at elevated temperature as well as resistance to other environmental effects.

For the past decade, research at United Technologies Research Center (UTRC) in the area of ceramic matrix composites has centered on systems based on the reinforcement of glass and glass-ceramic matrices with NICALON polymer derived SiC fibers. In the past few years, this research has concentrated on the study of the fiber/matrix interface and the relationship of the interfacial chemistry and morphology to the composite mechanical and thermal properties[44,47,50]. The characterization of the interfaces in these composites has been accomplished primarily by a combination of scanning electron microscope (SEM) observations of composite fracture surfaces, transmission electron microscope (TEM) replica and thin foil analysis, and scanning Auger microprobe (SAM) analysis of composite fracture surfaces. This work has enabled a greater understanding to be reached of the reactions that occur and the phases formed in these systems and has led to the

successful development of strong, tough, and oxidatively stable glass-ceramic matrix/NICALON fiber composite systems for use to temperatures approaching 1000°C. While the attainment of much higher use temperature glass-ceramic matrices has been demonstrated, the inherent formation of a carbon rich interfacial layer between the NICALON fibers and the glass-ceramic matrices during fabrication make the oxidative stability of these composites difficult to achieve in the temperature range of 1000-1300°C. Work in this area is being carried out at UTRC, primarily through the application of fiber coatings prior to composite fabrication.

In addition to the oxidative stability problems associated with the interfacial carbon layer formation in continuous NICALON fiber reinforced ceramic composites, another disadvantage of these fibers is that the fabrication temperature necessary to fully densify the ceramic matrices is often well above the upper temperature limit for stability of these fibers and can promote severe interaction between the fibers and constituents of the matrix. Also, the fabrication of near net shape components is much more difficult in the case of continuous fiber reinforcement than for discontinuous fiber, whisker, or particulate reinforcement.

It was thus decided to utilize the methods developed at UTRC and the experience gained during the aforementioned investigations into the fiber/matrix interface in Nicalon fiber composites and apply them to a comprehensive study of the chemistry and morphology of whisker/matrix interfaces in SiC and Si_3N_4 whisker reinforced glass-ceramic matrix composites. In particular, the effect of interfacial chemistry on the mechanical and thermal properties of the composites was investigated. The properties of interest include the strength and toughness of the composite as a function of temperature, the fracture mode of the composite, the mode of crack propagation, the effect of whisker coatings, as well as the composite oxidative stability. A major component of this investigation is a detailed study of the chemistry and morphology of the whisker/matrix interface through the use of analytical techniques such as scanning Auger multiprobe (SAM) of the various whiskers both before and after incorporation into composites and transmission electron microscopy (TEM) of polished sections and thin foils. These techniques have been previously utilized with great success in the study of continuous fiber reinforced glass and glass-ceramic matrix composite interfacial zones.

PART I - WHISKER COMPOSITES

II. BACKGROUND

With the recognized limitations of continuous fiber reinforced ceramic matrix composites as the major driving force, much work has been devoted in the past few years to the area of ceramic whisker reinforced glass, glass-ceramic, and ceramic matrix composites[1-34]. By far the greatest amount of work to date on whisker reinforced ceramics has dealt with SiC whisker reinforced ceramic matrices of Al_2O_3, mullite ($3Al_2O_3 \cdot 2SiO_2$), and, to a lesser extent, ZrO_2 and Si_3N_4[5-34]. From these studies, it was found that for materials that are supposedly similar, very different strength and fracture toughness values were obtained depending on the particular investigator. In general, significant toughness increases were found primarily in the alumina matrix systems. The mixed oxide systems containing zirconia also showed significant toughness values but much of this may be due to the transformation toughening afforded by the tetragonal to monoclinic zirconia phase change that occurs under stress. The particular type of SiC whisker utilized also appeared to influence the composite properties obtained.

Researchers at Corning Glass have studied the incorporation of whiskers into various glass and glass-ceramic matrices[1], and found that the strength and fracture toughness of these materials were improved significantly by the whisker additions. Similar studies at Los Alamos National Laboratories utilizing an variety of SiC whiskers in a borosilicate glass matrix[2] also found increases in RT strength and fracture toughness over the glass itself. No whisker/matrix interfacial studies were done and no attempts were made to alter or "engineer" the interfacial chemistry in either of these studies.

At UTRC, research into whisker reinforced ceramic matrix composites, prior to the inception of the current program, was confined primarily to the measurement of mechanical properties of glass matrix composites reinforced with Si_3N_4 whiskers[3] and glass and glass-ceramic matrix composites with SiC whiskers[4]. From this work, it was found that all SiC and Si_3N_4 whisker reinforced glass or glass-ceramic matrix composites exhibited linear stress-strain or load-deflection curves to the point of failure, and fractured into two halves in a relatively brittle fashion. The whiskers were found to strengthen the matrices but did not alter the brittle fracture nature appreciably. No interfacial chemistry studies were done as part of these

programs.

From the results of the first year's effort under the current AFOSR program[67], it became apparent that the chemistry and morphology of the various types of SiC and Si_3N_4 whiskers investigated played a very important role in determining the properties obtained when these whiskers were incorporated into lithium aluminosilicate (LAS) glass-ceramic matrices. The highest strength and toughness composites were obtained by utilizing SiC whiskers that exhibited as-received surfaces that, from SAM analyses, were high in carbon content. An additional requirement appeared to be that the whisker surface morphology should be relatively smooth and not exhibit abrupt changes in whisker cross-section. An example of this was the American Matrix, Inc. (AMI) SiC whiskers. While they exhibited a carbon rich surface, the morphology of these whiskers was so uneven in cross-section that the composites made from them did not exhibit high strength or toughness.

The SiC whiskers that exhibited relatively smooth and carbon rich surfaces, such as the ARCO, Tokai, and Tokai TWS-400 whiskers, tended to result in the highest strength and toughness LAS matrix composites. When whiskers that debonded from the matrix during fracture of these composites were analyzed in the SAM, it was found that the carbon rich nature of the whisker surface region had become even more carbon rich. Apparently, the mechanism as proposed by Cooper[49] whereby SiC can react with oxygen to produce silica plus carbon may be operative during processing of these composites. Indent cracks that were deliberately introduced into these composites were found to interact strongly with the whiskers, resulting in whisker/matrix debonding, crack bridging, and whisker pullout, all of which enhance the toughness of the composite. In contrast, the Los Alamos Nat. Lab (LANL) SiC whiskers, which initially exhibited surfaces that were relatively close to stoichiometric SiC, resulted in LAS matrix composites that showed very little evidence of whisker/matrix debonding, crack bridging, or whisker pullout, thus leading to very weak composites with low fracture toughness. The notching of the LANL whisker surfaces during composite fabrication, as found from TEM thin foil analysis, may also contribute to the low strength and toughness of these composites.

When Si_3N_4 whiskers were incorporated into LAS matrices, the resultant composite RT strength and toughness were found to be only moderate. The toughness increase found for this system appeared to be due to a reaction that occured during composite fabrication that resulted in the formation of a third phase at the whisker/matrix interface. This phase, which apparently acted as a crack deflector to some degree, has been investigated further during the past year

through TEM thin foil analysis and was found to consist of silicon oxynitride (Si_2N_2O) with some yttrium impurity. At elevated temperatures (1000°C), however, this composite system exhibited essentially no strength, due to nitrogen diffusion into the matrix causing the observed lack of matrix crystallization during heat-treatment. It is apparent that this system is not suitable for elevated temperature applications.

The emphasis for the continuation of this investigation during the past year was focused on the evaluation of SiC platelets as reinforcement for glass-ceramic matrices, the investigation of the effect of SiC whisker coatings such as carbon and BN on LAS matrix composite properties, fabrication and characterization of higher temperature calcium aluminosilicate (CAS) glass-ceramic matrix/SiC whisker composites, high resolution TEM studies of various SiC whisker/LAS matrix composite interfaces, and the characterization of composite fracture toughness (K_{IC}) as measured by three different methods; SENB, controlled flaw, and indentation crack length.

One of the motivations for the study of SiC platelets was the aspect of the health hazards associated with SiC whiskers. The SiC whiskers utilized during the past year were primarily the somewhat larger diameter Tokai TWS-400 whiskers, both coated and uncoated. These whiskers appeared to result in relatively strong and tough composites, but, due to their larger diameter, were considered to be easier and safer to handle. Correct environmental controls and safeguards are absolutely necessary when working with whiskers, and have been employed at UTRC during the performance of this program. However, it was decided towards the end of 1989 that the risks of working with whiskers were greater than the possible rewards, and that the effort under this program as of January, 1990 would transition towards the investigation of the interface in coated continuous fiber/glass-ceramic matrix composites. The results generated under this investigation are reported in Part II of this report.

PART I - WHISKER COMPOSITES

III. TECHNICAL DISCUSSION

A. Materials

The materials that are being investigated under this program are listed in Table I. The glass-ceramic matrices being utilized are LAS-I, LAS-A, and CAS. The LAS matrices both crystallize to β-spodumene and the CAS matrix to anorthite. LAS-I was utilized extensively during the first year of the program, while LAS-A (a more refractory version of LAS-I due to removal of trace amounts of Na, K, Nd, and Zn) and the CAS matrix were utilized during the past year of the program.

During the past year, the SiC whiskers under study consisted of the larger diameter (~1 μm) Tokai TWS-400 type, both uncoated and carbon coated, as well as BN coated small diameter (<0.7μm) ARCO whiskers. The carbon coated TWS-400C whiskers were received as-coated from Textron, Inc., Lowell, MA, while the BN coatings were applied by a CVD process a Synterials, Inc, Herndon, VA, on ARCO whiskers supplied by UTRC. In addition, a sample of SiC whiskers from Unocal, Brea, CA, were briefly examined. All of the coated and uncoated whiskers were analyzed in the SEM and SAM (except the UNOCAL SiC) in order to determine their morphology and their coating and/or near-surface chemistry. The SiC platelets were obtained from American Matrix, Inc., Knoxville, TN, in two size ranges, -200 and -325 mesh.

B. Sample Fabrication

The processing steps required to fabricate the LAS and CAS matrix/whisker composites were as follows. The required amount of glass powder (~8 μm average particle size) and whiskers were weighed out in an enclosed hood that was under negative pressure by means of a Nilfisk filtering system equipped with a Hepa filter. With the health hazards of small whiskers being of utmost concern, every attempt was made to ensure that the whiskers did not become airborne and any that did were trapped in the Hepa filter. All of the composites fabricated under the program were formulated to contain 30 vol% whiskers (36 wt% for the LAS matrix composites and 33.6 wt% for the CAS matrix composites).

After weighing, the whiskers and glass powder were mixed in a Szegvari attritor (Union Process Co., Akron, OH) using mullite balls and propanol as the fluid media. It was found that attriting at a low speed (100 RPM) for ~3 hrs resulted in an excellent dispersion of the whiskers and glass powder. After milling, the mix was dried in a large flat pan with care being taken after drying to break up the dried material by hand mixing. The glass powder/whisker mixes were then hot-pressed in graphite dies at temperatures of 1300-1350°C for 30 min for LAS and 1450-1500°C for 10 min for CAS under a pressure of 2 ksi (13.8 MPa). The LAS matrix/SiC platelet composites were fabricated in a similar manner. All of the hot-pressed composites were very close to full density.

After pressing, the composite panels were then cut into flexural test samples of dimensions ~0.2 x 0.1 x 3.0 inches (~0.51 x 0.25 x 7.6 cm). Those samples to be used for single edge notched beam (SENB) fracture toughness testing were sliced halfway through their thickness with a very thin diamond blade. Those composites to be tested in the "ceramed" or matrix crystallized condition were heat-treated in argon to 900°C for 24 hrs in order to crystallize the LAS matrices to a β-spodumene/silica solid solution phase having the β-quartz crystal structure, and to 1200°C for 24 hrs in order to crystallize the CAS matrices to anorthite.

C. SiC Platelets and Composites

As was mentioned in the previous annual report on this contract[67], SiC platelets of two different (-200 and -325 mesh) size ranges were obtained from American Matrix, Inc. (AMI). The morphology of these platelets are shown again in Figs. 1 and 2. From these figures, it appears that the larger size platelets tend to grow into one another during their fabrication, while the smaller size platelets appear to contain a considerable amount of particulate or fragmented platelets. Both of these platelet types were analyzed in the scanning Auger multiprobe (SAM) and found to be very close to stoichiometric SiC with a small amount of oxygen impurity, as shown in Fig. 3 for the smaller -325 mesh platelets. A very slight enrichment of both C and O was found on the surface of the platelets. The C is most likely due to adsorbed organic impurities while the O is undoubtedly due to a slight oxidation of the exposed SiC surface.

LAS-I matrix composites with 30 vol% SiC whiskers were fabricated utilizing both the -200 and -325 mesh whisker sizes. The results of RT flexural and SENB fracture toughness tests on these composites are shown in Table II, along with values for unreinforced Corning 9608 LAS material, which is basically identical to

the LAS-I matrix composition and ceramed crystal structure. In contrast to the SiC whisker composite data (except for the Los Alamos whiskers) presented in the previous annual report, the SiC platelet composites did not show a RT strength increase over the unreinforced LAS. Due to these low strengths, no elevated temperature testing was done. The measured RT fracture toughness values, however, showed that the critical stress intensity factor (K_{IC}) of the composite materials was about twice that of the unreinforced LAS. This increased resistance to crack propagation can be seen visually from Fig. 4, which shows the fracture surface of the LAS-I matrix/-200 mesh SiC platelet composite #144-89. While there is no evidence of actual platelet pullout, and thus probably no crack bridging contribution to toughness, there is significant evidence of matrix crack diversion due to the platelets and also matrix/platelet interfacial debonding when the platelets are aligned with or at an angle of ~45° or less to the crack plane.

A SAM depth profile of a platelet surface on the fracture surface of the -325 mesh SiC platelet/LAS-I matrix composite #220-89 was obtained and is shown in Fig. 5. It can be seen from this figure that the original platelet near-surface composition (Fig. 3) has been retained in the composite. No tendency to form a carbon rich interfacial layer was evident, unlike the carbon rich SiC whiskers analyzed previously. The SEM micrographs in Fig. 5 show the actual platelet surface analyzed, both before and after Ar ion sputtering to a depth of 1000Å. The analysis was done at a point in between the rough appearing matter adhering to the platelet surface. After the 1000Å sputter, the rough adhering matter, which is small matrix particles, has been cleaned off the platelet surface.

While the bonding between the SiC platelets and the LAS matrix is apparently quite strong, crack deflection and a significant amount of matrix/platelet debonding does occur, undoubtedly enhanced by the tensile stresses generated at the interface due to the difference in thermal expansion coefficients between the LAS matrix [$\alpha = 1 \times 10^{-6}/°C$ (ceramed) to $3 \times 10^{-6}/°C$ (as-pressed)] and the SiC platelets ($\alpha = 4.5 \times 10^{-6}/°C$).

D. Unocal SiC Whiskers

A small sample of SiC whiskers was received from Tom Coyle of Unocal, Inc. for evaluation. These whiskers are developmental and are designed to have diameters of greater than 2 μm, thus minimizing their health hazards compared to the smaller sub-micron whiskers. Unfortunately, SEM analysis of the morphology of these whiskers, as shown in Fig. 6, indicated that very few of the whiskers were straight, with the majority being curved with a "wormy" type of appearance. It was

thus decided not to fabricate a composite or pursue the characterization of these whiskers further due to their lack of straightness.

E. Coated SiC Whiskers and Composites

Two different types of coated SiC whiskers were evaluated during the past year. One of these was carbon coated Tokai TWS-400C whiskers while the other was CVD BN coated ARCO SiC whiskers, with the latter coating being applied to UTRC furnished whiskers by Synterials, Inc. The purpose of this investigation was to determine the effect of a deliberately applied weakly bonded whisker/matrix interface on the composite properties.

1. Carbon Coated SiC Whiskers and Composites

The SAM depth profile to a sputter depth of 2000Å for the carbon coated Tokai TWS-400C SiC whiskers in the as-received condition is shown in Fig. 7. It can be seen that the carbon coating applied to these whiskers by the manufacturer is extremely thin (<100Å). The whisker chemistry under the surface carbon coating is essentially identical to the composition found for the uncoated TWS-400 whiskers, as was shown in Fig. 3 of the previous annual report. These whiskers, like other Tokai and Arco SiC whiskers investigated, are distinctly rich in carbon in their near-surface region, being ~55-60 at% C, 40-45% Si, as determined from SAM analyses.

An LAS-I matrix composite containing 30 vol% (36 wt%) of the carbon coated Tokai TWS-400C SiC whiskers was fabricated utilizing the processing conditions discussed in a previous section. The flexural strength and RT fracture toughness of this composite (#308-89) are shown in Table III, along with values obtained previously for uncoated Tokai TWS-400 SiC whiskers in LAS-I (and the BN coated SiC whisker composite to be discussed in the next section). From Table III, it can be seen that the RT flexural strength in both the as-pressed and ceramed condition and the 800°C ceramed strength are relatively high, but not quite as good as the uncoated Tokai TWS-400 SiC whisker composite (#718-88). All test values represent single tests, due to the small size of the composites and the number of tests conducted on each composite. The RT SENB fracture toughness values are essentially the same for both composites. The flexure strength of the composite did not decrease as a result of a flowing oxygen heat-treatment at 550°C, indicating that if the carbon coating is still present at the whisker/matrix interface, it is not susceptible to oxidation under these conditions. Continuous NICALON fiber reinforced LAS matrix composites, which form a carbon rich interfacial layer of ~200-400Å in thickness during composite fabrication, degrade significantly in

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strength after the same oxidation exposure due to oxidation of the interfacial carbon layer[47,50].

Figure 8 shows the RT fracture surface for composite #308-89 in the as-pressed condition. It can be seen that the fracture surface is quite rough with a significant amount of whisker/matrix debonding and whisker pullout. Figure 9 shows the crack paths due to an indent load on the surface of a polished and etched surface of the composite. A large amount of crack deflection and crack bridging are evident, as well as the whisker/matrix debonding and whisker pullout observed on the composite fracture surface. All of the above mechanisms contribute to the increased toughness noted for this composite.

Figure 10 shows the SAM depth profile obtained on a whisker surface that was exposed on the fracture surface of composite #308-89. Comparing this figure to that of the as-received carbon coated whiskers (Fig. 7), it is evident that the carbon coating is still on the whiskers after composite fabrication, although it must be remembered that uncoated Tokai TWS-400 SiC whiskers in LAS-I formed an almost identical carbon interfacial layer, as was shown in Fig. 15 of the previous annual report. As with the uncoated whiskers, a significant amount of oxygen diffusion into the whisker surface region has occurred during composite fabrication.

TEM thin foils of composite #308-89 were prepared by ion beam milling. Figure 11 shows a low and high magnification micrograph and selected area electron diffraction (SAED) patterns for the amorphous as-pressed LAS matrix and the SiC whiskers, most of which exhibited a characteristic diffraction pattern for β-SiC. The whisker/matrix interface in the high magnification view appears to show some sort of very thin interfacial structure, although this could be interpreted simply as an artifact from the thinning process or a slightly mis-aligned whisker. However, as will be shown in a later section on the high resolution TEM (HRTEM) of three different whisker composites as performed by Prof. Steve Nutt of Brown University, this particular composite does indeed exhibit a very thin (~40Å) interfacial phase of a mixture of amorphous and graphitic carbon. This finding supports the SAM observation of a retained carbon layer on the whisker surfaces.

2. BN Coated SiC Whiskers and Composites

BN coatings applied by a CVD process to continuous length NICALON, graphite, or alumina fibers have been shown to result in improved strength and toughness over uncoated fibers when the fibers were incorporated into a variety of ceramic matrices including silica, SiC, zirconia, and cordierite[68]. The BN coating

on the fibers was thought to limit both the physical bonding and chemical interactions between the fibers and matrix. BN coatings on continuous fibers in glass-ceramic matrices are being evaluated at UTRC under the current AFOSR contract, as will be discussed in the second phase of this report.

In order to evaluate the effect that a weakly bonded artificially deposited whisker coating such as BN could have on the properties of a SiC whisker/LAS matrix composite, a batch of Arco SC-9 SiC whiskers was sent to Synterials, Inc, Herndon, VA for the deposition by CVD of ~2000Å of BN. It was originally planned to utilize the LANL SiC whiskers for BN coating, since they exhibited rather strong bonding and no carbon interface formation when incorporated into LAS matrices, but not enough LANL whiskers were available for BN coating.

The as-coated SiC whiskers received from Synterials are shown in Fig. 12. Unfortunately, many of the whiskers were apparently agglomerated into bundles prior to coating with the result being that whiskers that were at or near the surface of a whisker bundle were coated with BN while those near the interior of the bundles were either not coated or coated very thinly, as can be seen from Fig. 12. A BN coated whisker near the surface of a bundle was analyzed in the scanning Auger, with the result being shown in Fig. 13. While this particular whisker exhibited a coating of ~1000-1500Å in thickness, the coating was heavily contaminated with carbon. Carbon (and oxygen) are often found in BN coatings applied by CVD at relatively low temperatures, but this amount of carbon was extremely high and not typical of other BN coatings investigated at UTRC on continuous fibers.

An LAS-I matrix composite (#335-89) was fabricated utilizing the BN coated SiC whiskers. During attrition milling of the whiskers and matrix glass powder, it could be expected that most of the agglomerated whisker bundles would be broken up. Figure 14 shows the fracture surface of this composite, while the mechanical properties are listed in Table III, along with the previously fabricated and characterized uncoated Arco SiC whisker composite #289-88. From Fig. 14, it can be seen that the composite fracture surface is relatively rough, with some exposed whisker surfaces that appear rather rough themselves, although the number of pulled out whiskers and whisker/matrix debonds appears to be less than that normally seen in an uncoated Arco SiC whisker composite. The flexural strength of this composite, as shown in Table III, is on the order of half that of the uncoated whisker composite #289-88 at both RT and 800°C. The RT fracture toughness of ~3.3 MPam$^{1/2}$ is substantially higher than the unreinforced LAS matrix alone (0.85 MPam$^{1/2}$), but about 30% lower than the fracture toughness measured for the uncoated Arco SiC whisker composite #289-88.

From the indent crack growth SEM micrograph for composite #335-89, as shown in Fig. 15, it can be seen that the propagating crack is certainly diverted by the presence of the BN coated SiC whiskers, but possibly not as much as was previously found for uncoated or carbon coated Arco or Tokai SiC whiskers (see Fig. 9). The reason for this may be due to the large amount of interdiffusion noted between the matrix and the BN coating, as shown in the SAM analysis of a rough or fuzzy appearing whisker surface on the fracture surface of composite #335-89 in Fig. 16, leading to increased bonding between the matrix and whisker over that for uncoated whisker composites that form a carbon rich interface. From Fig. 16, it can be seen that the BN coating (which originally contained a large amount of carbon) now exhibits a complex chemistry of a mixture of BN plus carbon as well as significant amounts of oxygen, silicon, and aluminum. TEM thin foil analysis confirms the complex chemical nature of the BN coating in the composite, as shown in Fig. 17 for a somewhat agglomerated group of coated whiskers in composite #335-89. The coating appears to contain microcrystallites (100-250Å grain size) of BN surrounded by a silicate glassy phase. From the energy dispersive X-ray spectroscopy (EDX) patterns shown in Fig. 17 for the interface, matrix, and whiskers, Al and possibly some Mg are present in the interfacial region, while oxygen can be detected in the whiskers, confirming the SAM data. Carbon, while undoubtedly present in the interface and definitely present in the SiC whiskers, is difficult to detect in the presence of Si by this analysis method due to absorption of the carbon X-rays by the Si.

From the results of these experiments with BN coated SiC whiskers in an LAS matrix, it appears that this method of engineering a deliberately weakly bonded interface is not promising. However, the fact that the whiskers were unevenly coated due to agglomeration and that the BN coating applied contained a large amount of carbon may have contributed to the disappointing properties. But, since the use of carbon rich SiC whiskers in LAS matrices produces a very high carbon containing, weakly bonded interface during composite processing that is very thin and not interconnected and thus resistant to oxidation, an artificially created interface such as BN may not offer any advantages in this particular composite system. BN coatings on continuous fibers such as NICALON in glass and glass-ceramic matrices may, however, be very advantageous for controlling and optimizing fiber/matrix interfacial bonding and environmental resistance.

F. Si_3N_4 Whisker Composite TEM Studies

As mentioned in the background section of this report and discussed in detail in

the previous annual report[67], an LAS-I matrix composite was fabricated utilizing UBE Si_3N_4 whiskers that exhibited moderate strength and toughness values at RT, but essentially no strength at 1000°C due to nitrogen diffusion into the matrix preventing matrix crystallization. From TEM replica analysis of a polished composite cross-section, it appeared that a thin reaction layer had formed at the whisker/matrix interface during composite processing. During the past year, this composite was subjected to TEM thin foil analysis in order to determine the nature of this reaction.

Figure 18 shows thin foil micrographs, a SAED pattern for the interfacial reaction phase, and EDX analyses of the whiskers and the interfacial phase. From this data, it was determined that the interfacial reaction phase consisted of microcrystalline silicon oxynitride (Si_2N_2O) containing minor amounts of aluminum and yttrium impurities. The thickness of this phase around the whiskers appeared to vary somewhat but was on the order of 500-1000Å. Yttrium was listed by the manufacturer as an impurity in the whiskers at a level of 0.33 wt%. No yttrium was detected within the whiskers by EDX analysis, but was found in the silicon oxynitride reaction phase at a very low level. The vertical scale for the EDX analysis showing the presence of yttrium in the interface was much greater (~40X) than that showing the Si, Al, O, and N.

From previous studies dealing with interfacial characterization of Dow Corning HPZ fiber, which contains Si, N, and small amounts of C and O, in LAS-I glass-ceramic matrix composites[50], it was found that a silicon oxynitride interfacial reaction phase formed during composite fabrication, as well. It thus appears that silicon nitride type fibers or whiskers are not particularly good reinforcing phases for LAS matrix composites due both to nitrogen diffusion into the matrix preventing matrix crystallization and the relatively good bonding characteristics of the silicon oxynitride phase to the matrix. Diffusion barrier and weakly bonded coatings applied to these types of reinforcing phases may allieviate the above problems, however, and will be investigated on HPZ fibers under the AFOSR fiber coatings effort.

G. Calcium Aluminosilicate (CAS) Glass-Ceramic Matrix Composites

Tokai TWS-400 SiC whiskers were utilized to fabricate a composite with a CAS matrix rather than the usual LAS matrix, in order to determine if the more refractory CAS matrix would result in a composite with good mechanical properties to a higher temperature and if the change to a matrix with different chemistry would

have an effect on the whisker/matrix interfacial composition and bonding characteristics. The CAS composition was formulated to result in the crystallization of anorthite ($CaO \cdot Al_2O_3 \cdot 2SiO_2$), which has a melting point of 1550°C, about 125° to 200°C higher than the β-spodumene-silica solid solution LAS glass-ceramic phases. Thus, hot-pressing temperatures needed to flow the CAS glass around the SiC whiskers were on the order of 200°C higher than that necessary for LAS matrix composites. Researchers at Corning Glass have used similar CAS compositions to fabricate both SiC whisker and SiC fiber reinforced composites[69].

1. Mechanical Properties and Fracture Behavior

Figure 19 shows the fracture surface of the CAS matrix/Tokai TWS-400 matrix composite (#499-89) in the as-pressed condition. From this figure, it can be seen that the fracture characteristics of this composite show a significant amount of whisker/matrix debonding, whisker pullout, and crack diversion that appears to be within the matrix itself. The RT flexural strength of this composite was 276 MPa (40 ksi), somewhat less than the 358 MPa (52 ksi) for the same whiskers in an LAS matrix.

A polished and HF etched surface of this composite was indented and the crack path examined in the SEM, as shown in Fig. 20. It can be seen that there is a considerable amount of crack bridging by the SiC whiskers, accompanied by whisker/matrix debonding. There also appears to be angular shaped particles in the composite microstructure that are not SiC whiskers. X-ray diffraction analysis was conducted on crushed samples of this composite in the as-pressed condition and after a 1200°C, 24 hr, Ar heat-treatment in order to completely crystallize the matrix to anorthite. Figure 21 shows the results of the X-ray diffraction analysis. From these results, it is apparent that the as-pressed and ceramed composites exhibit virtually identical crystalline phase assemblages, and that there is α-alumina present in the matrix of both samples. On further examination of the CAS phase diagram, it became apparent that the CAS composition used for composite #499-89 (40.2 wt% SiO_2, 38.7% Al_2O_3, 18.1% CaO, 2.0% ZrO_2, 1.0% As_2O_3) was slightly off stoichiometric anorthite towards the alumina corner of the phase diagram. Thus, it is not surprising that some alumina crystallized in the matrix on cooling from the fabrication temperature.

Table IV compares the flexural strengths and RT fracture toughness values obtained for the CAS and LAS-I matrix composites, both with Tokai TWS-400 SiC whiskers. While the RT flexural strength of the CAS matrix composite #499-89 in the as-pressed and ceramed condition is somewhat lower than the LAS-I matrix

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composite #718-88, the elevated temperature (1000°C) strength is significantly lower. The CAS matrix composite was expected to retain its strength to a higher temperature than the LAS matrix composite. In contrast, the RT fracture toughness values obtained on the CAS matrix composite were somewhat higher than the LAS matrix composite. In fact, the K_{IC} value of 5.05 MPam$^{1/2}$ obtained for the as-pressed CAS matrix composite is the highest yet obtained on this program for any whisker reinforced glass-ceramic. No obvious reason for the low 1000°C strength for this composite could be determined.

2. TEM Characterization of CAS Matrix/SiC Whisker Composite

TEM replicas of polished cross-sections of composite #499-89 in both the as-pressed and ceramed conditions were prepared, as well as thin foils of the composite in the as-pressed condition. Figures 22 and 23 show the TEM replica characterizations of the as-pressed and ceramed composites, respectively. As could be anticipated from the previously shown X-ray patterns, the microstructures of both of these samples are essentially identical. Upon etching the polished samples with HF, the SiC whiskers and the alumina particles in the matrix both appear smooth and stand out from the more striated appearance of the anorthite phase. Very little, if any, residual glass phase is apparent in the matrix, which further complicates the reasoning of why the 1000°C strength of this composite was so low.

TEM thin foil analysis of the as-pressed composite, as shown in Figs. 24 and 25, verified the observation that virtually no residual glassy phase is present in the matrix. In Fig. 24 the three crystalline phases present in the matrix can be seen, along with their EDX spectra; phase A being alumina, B being anorthite, and C being a SiC whisker. Figure 25 shows a different area of the thin foil, with the three phases of alumina, anorthite, and SiC and their associated selected area electron diffraction patterns. No amorphous or glassy matrix phase could be found. Also, no apparent interaction between the matrix phases and the SiC whiskers could be seen, at least at the magnifications investigated.

It thus appears that the CAS matrix composite #499-89 exhibits an essentially crystalline matrix that forms on cooling from the composite fabrication temperature of 1500°C, and that additional heat-treatment or "ceraming" at 1200°C for 24 hrs does very little to the matrix phase assemblages. One distinctive difference noted when examining the crystalline CAS matrices in thin foil in the TEM compared to crystalline LAS matrices, is that the crystalline β-spodumene-silica solid solution LAS phase vitrifies, or becomes amorphous, under the electron beam, whereas the crystalline CAS anorthite phase does not.

3. Scanning Auger Analysis of CAS Matrix Composites

A fractured surface of a RT as-pressed flexural sample was characterized in the scanning Auger multiprobe (SAM) for the near-surface chemistry of a SiC whisker surface that was exposed on the fracture surface. Since matrix/whisker debonding was quite prevalent for this sample, an exposed SiC whisker from which the CAS matrix had pulled away from was quite easy to find.

It was expected that the SAM depth profile of an exposed whisker surface would show the formation of a carbon rich whisker/matrix interface, similar to that found previously for the Tokai TWS-400 whiskers in an LAS matrix, especially in light of the high fracture toughness and large amount of whisker/matrix debonding noted for this system. However, no enrichment of carbon on the SiC whisker surface was found, as shown in Figure 26. A considerable amount of oxygen and a small amount of calcium were found to have diffused into the whisker during composite fabrication. Since this result was quite unexpected, a second sample from this composite was freshly fractured and a whisker surface located. In order to determine if the carbon rich layer may have stuck to the matrix surface instead of the whisker surface upon composite fracture, a matrix trough from which a whisker had been extracted was also located and depth profiled.

The SAM analysis of the whisker surface and matrix trough are plotted together in Fig. 27. As can be seen from Fig. 27, the whisker surface composition was basically the same as the first sample analyzed, with somewhat more oxygen and aluminum diffusion being noted but again no surface carbon rich layer was present. While some diffusion of carbon was noted into the matrix to a depth of ~500Å and a somewhat silica rich layer appeared to be present on the trough surface, no carbon rich layer was found. It is possible that upon fracture of the composite and subsequent pullout of the whisker from the matrix, the rather weak carbon layer simply disintegrated, although the retention of the carbon interfacial layer on composite fracture has always been seen to occur in other composites that undergo this particular interfacial reaction. Or it may be, as discussed by Cooper and Chyung[49], that the oxidation reaction of the initially carbon rich SiC during composite fabrication to form additional solid carbon does not occur as readily in the less basic alkaline earth CAS system as it does in the alkali LAS system. High resolution TEM (HRTEM) of this composite system would be necessary to determine if a distinct carbon rich layer exists in this system and this was not accomplished during this reporting period.

H. High Resolution TEM (HRTEM) Studies of LAS Matrix/SiC Whisker Composites

During this past reporting period, HRTEM studies of two composites discussed in the last annual report (#290-88-LAS-I/Tokai SiC whiskers, and #359-88-LAS-I/LANL SiC whiskers) and one composite (#308-89-LAS-I/carbon coated Tokai TWS-400C SiC whiskers) discussed previously in this report, were conducted by Prof. Steve Nutt of Brown University, Providence, RI, on composite thin foils supplied by UTRC. From previous scanning Auger studies at UTRC, both composites #290-88 and #308-89 were found to have a very thin (~150Å and 50Å, respectively) carbon rich whisker/matrix interfacial layer and exhibited high strength and fracture toughness. In contrast, the LANL SiC whisker composite #359-88 was found from SAM analysis not to exhibit an interfacial high carbon layer and gave low strength and toughness values. TEM thin foil studies at UTRC at magnifications up to 255,000X were not sucessful in definitively showing whether or not a carbon rich interfacial phase did or did not exist in these composites. The TEM that Prof. Nutt utilized for his HRTEM investigations was a JEOL JEM-2010, which is a 200kv state-of-the-art instrument with a more sophisticated lens design and the capability of atomic resolution imaging, when compared to the Phillips EM-400 120kv TEM at UTRC.

Figure 28 shows the HRTEM microstructure at the whisker/matrix interface of the LAS-I matrix/Tokai SiC whisker composite #290-86 at a magnification of 400,000X. A distinct amorphous appearing interfacial zone of ~150Å in thickness can be seen, which corresponds quite well with the SAM depth profile of a whisker fractured from this composite, as was shown in Fig. 14 of the previous annual report, that indicated a carbon rich interfacial layer on the order of the same thickness. A low atomic number thin window detector was not employed during the HRTEM analysis, so identification of this layer as rich in carbon is not positive. It was noticed during the HRTEM analysis that not all whisker/matrix interfaces in this composite exhibited as distinct an interfacial layer as shown in Fig. 28. It may be that the formation of this layer is affected by local chemical imhomogeneities present in the LAS matrix or possibly by the crystalline orientation of the whisker surface.

Figure 29 shows the interfacial microstructure as determined from HRTEM of two different regions in the LAS-I matrix/carbon coated Tokai TWS-400C SiC whisker composite #308-89. The SAM depth profile of this composite was

presented earlier in Fig. 10 as was the thin foil TEM microstructure obtained at UTRC. Figure 29A shows a very uniform interfacial layer of ~50Å in thickness, which corresponds quite well with the carbon rich layer thickness determined from SAM analysis. On close inspection, it can be seen that the outer part of this interfacial layer appears to be graphitic in structure, while the part next to the SiC whisker appears amorphous. In Fig. 29B, no distinct interfacial layer can be seen. However, the ~150Å wide region between the small nucleation particle of ZrO_2 (plus impurities of As, Fe, and Co) is distinctly graphitic in nature. As in the previous composite, not all of the whisker/matrix interfaces exhibited a distinct interfacial layer. It appears that during processing of the composites, those that form carbon rich interfacial layers from the "carbon-condensed" oxidation displacement reaction:

$$SiC + O_2 = SiO_2 + C \qquad (1)$$
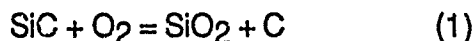
as proposed by Cooper and Chyung[49], do so only at certain interfacial areas, while those that start with thin carbon coatings already on the SiC whisker surfaces can experience coalescense of the carbon layers to lower energy sites such as between small matrix particles close to the whisker surface and the whisker surface itself, as was seen in Fig. 29B.

Figure 30 shows a typical HRTEM interfacial microstructure for the LAS-I matrix/Los Alamos National Lab (LANL) VLS grown SiC whisker composite #359-88. As was shown in the TEM thin foil micrograph of Fig. 27 in the previous annual report, appendages or facets can be seen that appear to have grown laterally from the whisker surface during composite fabrication. No evidence of a distinct interfacial layer was found. Most of the appendages appear to be associated with the defect structure, or twinning, within the SiC whiskers. High resolution SEM of as-received LANL whisker surfaces, also done by Prof. Nutt at Brown Univ., showed no evidence of these appendages or facets or any notching of the whisker surface.

Faceting of LANL SiC whiskers has been found previously by Nutt and Phillips[32] for hot-pressed Si_3N_4 matrix/SiC whisker composites and by Schoenlein, et al[33] for RBSN matrix/SiC whisker composites. In the hot-pressed silicon nitride matrix composites, faceting was found to occur to a greater degree at the higher curvature region of the rounded triangular cross-section whiskers. In the RBSN matrix composites, it was found that the lowest strength and toughness composites were those in which the LANL SiC whisker surface faceting was the most pronounced. The low LAS matrix composite strength found in the present

study for the LANL SiC whiskers, compared to Arco or Tokai SiC whisker composites, may have much more to do with the appendage growth or faceting of the whisker surfaces during composite fabrication than it does to the lack of an interfacial carbon rich layer. That relatively low composite strength was also found for the AMI SiC whiskers in LAS-I, which formed a carbon rich interfacial layer but started with whiskers that had a very rough surface morphology, argues for the importance of a smooth whisker surface such that whisker/matrix interfacial sliding can occur and no stress concentrators can exist.

HRTEM of the CAS matrix/Tokai TWS-400 SiC whisker composite #499-89 that showed no interfacial carbon rich layer from SAM analysis but exhibited relatively high RT flexural strength and very high RT fracture toughness is scheduled, but was not completed in time to be included in this report. When this is accomplished, a publication will be submitted to the Journal of the American Ceramic Society, co-authored by J.J. Brennan and S.R. Nutt, with the tentative title of "The Influence of Interface Structure and Chemistry on the Properties of Glass-Ceramic Matrix/SiC Whisker Composites".

I. Comparison of Composite Fracture Toughness Measurement Techniques

The LAS and CAS matrix composite fracture toughness (K_{IC}) values presented in Tables II, III, and IV, were determined from single edge notched beam (SENB) tests, utilizing the methods and equations developed by Brown and Srawley[70]. Other methods to determine fracture toughness of brittle materials that require less sample machining and preparation are the indent techniques[71-75] that utilize a Vickers indent to initiate cracks, the length of which can then be correlated to the material fracture toughness, and the controlled flaw, or indentation strength method[76] that uses a Vickers indent to introduce flaws into the tensile face of a bend sample. It was decided to use the indent method and equations as developed by Marshall and Evans[74] and the controlled flaw method and equations developed by Chantikul, et al[76], along with the previously used SENB method to characterize the fracture toughness of three different SiC whisker composites; an LAS-A matrix/Tokai TWS-400 SiC whisker composite (#646-89), a CAS matrix/Tokai TWS-400 SiC whisker composite (#645-89), and a CAS matrix/carbon coated Tokai TWS-400C SiC whisker composite (#644-89).

The parameters utilized to determine K_{IC} from the indent method are the elastic modulus, indent load, average of the four crack lengths, and average of the four

indent lengths. For the controlled flaw method one needs only to determine the elastic modulus, Vickers hardness, indent load, and the subsequent flexural strength. At RT, the un-notched flexural strength, the SENB and controlled flaw flexural strength, and the SENB, indent, and controlled flaw K_{IC} were determined for the three composites. At elevated temperature (800°C), the SENB and controlled flaw K_{IC} and flexural strength were determined. For the indent tests, an indent load of 100 kg was utilized to insure that the crack length/indent length (c/a) was greater than two, as recommended by Anstis, et al[73], and for the controlled flaw tests an indent load of 65 kg was utilized

The results of these tests are shown in Table V. It can be seen that the RT flexural strength of the CAS matrix composites are somewhat higher than the LAS matrix composite, with the carbon coated whisker composite being the highest, in contrast to the previous composites #718-88 and #499-89 where the LAS matrix composite strength was highest. The RT fracture toughness values as measured by the SENB and controlled flaw techniques are very similar for each individual composite, with the CAS matrix composites exhibiting a somewhat higher toughness than the LAS matrix composite, as was found previously from SENB tests on composites #718-88 and #499-89. The indent technique gave somewhat higher values of toughness for the uncoated SIC whisker LAS and CAS matrix composites than the other methods, but a substantially lower value for the carbon coated SIC whisker/CAS matrix composite. Figure 31 shows typical fracture characteristics of the LAS matrix composite #646-89 for the three different methods of fracture toughness testing.

The calculated RT flexural strengths of the composites with either the notches cut into them for the SENB tests or the indent flaws on the tensile surfaces were on the order of 35-50% of the un-notched flexural strengths (taking into account the reduced thickness of the SENB samples due to the notch cut into them), with the controlled flaw samples being slightly lower in strength, probably due to the sharper crack introduced by the indent compared to the 7 mil diamond blade. These results are in contrast to those found at UTRC for the RT flexural strength of either discontinuous[77] or continuous[78] NICALON fiber/LAS matrix SENB composite samples where the notched strengths were from 78-90% of the un-notched values. Thus, the whisker composites are significantly more notch sensitive than comparable NICALON fiber reinforced LAS matrix composites.

The elevated temperature (800°C) fracture toughness tests were performed on the SENB and controlled flaw samples. No method of performing indent testing at 800°C was availalble. The results of these tests were generally cumparable to the

RT testing by these methods, except for the 800°C SENB tests on the two CAS matrix composites, which gave K_{IC} values of ~ 1 MPam$^{1/2}$ less that the controlled flaw tests. No obvious reason for the lower values found for the CAS matrix composites is evident, except that these samples were ceramed proir to testing and that previous CAS n... trix composite ceramed RT K_{IC} results (Table IV) gave lower fracture toughness values than the as-pressed composite.

The flexural strengths at 800°C for the SENB and controlled flaw samples were, in general, similar to the RT strengths determined from these tests for all of the composites. Not enough specimens from each composite panel were available for un-notched flexural testing to be done at 800°C, but for the LAS composite system, at least, previous results for a similar composite (#718-88) gave an un-notched 800°C flexural strength of 358 MPa (52 ksi). Thus, the notched or indented 800°C flexural strength for this sample was ~38% of the un-notched value.

From the results of the fracture toughness testing, it can be concluded that for these types of composite materials, the controlled flaw (or indent strength) method of testing appears to result in more consistant critical stress intensity values at both RT and elevated temperature. The main advantages over SENB testing are simpler sample preparation (no notch machining) and the presence of a sharp crack. While only one test per sample can be obtained, when compared to the indent technique, controlled flaw testing can easily be done at elevated temperatures and does not require microscopic measurement of crack length, the ambiguities of which may be responsible for tne wider range of fracture toughness values measured by the indent method.

PART I - WHISKER COMPOSITES

IV. CONCLUSIONS

During the past year's effort on interfacial studies of whisker reinforced glass-ceramic matrix composites, investigations focused on the evaluation of SiC platelets as a less hazardous reinforcement than whiskers, the investigation of the effect of SiC whisker coatings such as carbon and boron nitride on LAS matrix composite properties, fabrication and characterization of calcium aluminosilicate (CAS) matrix/SiC whisker composites, TEM studies of previously fabricated LAS matrix/silicon nitride whisker composites, high resolution TEM (HRTEM) studies of a variety of SiC whisker/LAS matrix composite interfaces, and the characterization of composite fracture toughness (K_{IC}) as measured by three different techniques; single edge notched beam (SENB), controlled indentation flaw, and indentation crack length.

From the results of the LAS matrix/SiC platelet composite characterization, utilizing two different sized platelets (-200 and -325 mesh), it can be concluded that the addition of SiC platelets to the LAS matrix does not result in an increase in strength, but does increase the toughness by a factor of two over the unreinforced LAS matrix. SAM depth profiling of the as-received platelets showed that they were essentially stoichiometric SiC which did not form a carbon rich platelet/matrix interface during composite fabrication. While bonding at the platelet/matrix interface was apparently relatively strong, enough crack deflection and matrix/platelet debonding of platelets aligned at angles of 45° or less to the crack plane did occur, resulting in the increased fracture toughness. Tensile stresses generated at the interface due to thermal expansion mismatch between the platelets and the matrix may have enhanced the tendency for interfacial debonding.

From the results of carbon coated Tokai TWS-400C SiC whisker/LAS matrix composite studies, it was found that the initial carbon coating applied by Tokai of less than 100Å remained at the whisker/matrix interface after composite processing. However, uncoated Tokai TWS-400 SiC whiskers were also found to form a carbon rich interfacial layer of approximately the same thickness after composite processing. Both of these composite configurations resulted in high strength, high fracture toughness materials with a significant amount of whisker crack bridging, whisker/matrix debonding, whisker pullout, and crack deflection

contributing to the toughness. Oxidative stability of the carbon coated whisker composite at a temperature (550°C) below which SiC oxidizes to silica, but above which carbon readily oxidizes to CO, was excellent. From the above observation, however, no advantage of precoating the whiskers with carbon was evident, at least for the composite types investigated.

The BN coated Arco SiC whiskers, as coated by Synterials, Inc., gave rather disappointing results as far as composite strength and toughness when incorporated into an LAS matrix. However, the fact that the whiskers were unevenly coated due to agglomeration and that the BN coating applied contained a large amount of carbon may have contributed to the relatively poor properties. In addition, the BN coating was shown to have reacted during composite processing to form a mixture of microcrystalline BN plus a silicate glassy phase. This complex interface may have actually resulted in increased bonding of the whiskers to the matrix over uncoated SiC whiskers. A high purity, stoichiometric, evenly deposited BN coating may be necessary to achieve the optimum interface. Even then, a coating of this type may be much more important for controlling and optimizing fiber/matrix interfacial bonding and environmental resistance for continuous fiber composites than for whisker composites.

The results of the investigation of calcium aluminosilicate (CAS) matrix/Tokai TWS-400 SiC whisker composites were somewhat disappointing and rather confusing. The particular CAS composition utilized was slightly alumina rich, so that the crystalline matrix consisted of a mixture of anorthite and alumina. Even though the RT flexural strength of the composite was found to be reletively high, the 1000°C strength was low. This result was surprising since TEM studies of the matrix showed essentially no glassy phase; only anorthite and alumina crystals. The other surprising result was that, while the RT fracture toughness (K_{IC}) was very high, SAM analysis showed no carbon layer existing at the whisker/matrix interface, as had been found previously for these whiskers in LAS matrices. High resolution TEM will be necessary to definitely characterize the phases present at the interface of this composite.

High resolution transmission electron microscopy (HRTEM) of LAS matrix/Tokai, carbon coated Tokai, and Los Alamos National Lab (LANL) SiC whisker composites conducted by Prof. Steve Nutt of Brown University, showed that a very thin (~50Å) distinct amorphous plus graphitic interfacial layer existed in the LAS matrix/carbon coated Tokai SiC whisker composite, as found from SAM analysis, but was not present at every interface. A similar amorphous layer of ~150Å thickness was seen in the uncoated Tokai SiC whisker composite, but was not positively identified as carbon, and again did not exist at all interfaces. The

thickness of the layer seen, however, did correlate well to the carbon rich layer found from SAM analysis for this composite. No evidence of any interfacial layer was found for the LANL SiC whisker composite, similar to that observed from SAM analysis, but severe faceting or appendage growth on the sides of the whiskers could be seen. This faceting phenomenon of the LANL whiskers during composite fabrication may actually have much more to do with the very low strength and low fracture toughness of these composites than the lack of an interfacial carbon rich layer, since the very rough nature of the surface of these whiskers would prevent interfacial sliding and could act as severe stress concentrators.

From the results of fracture toughness testing of LAS and CAS matrix composites utilizing the single edge notched beam (SENB) method, the indent method, and the controlled flaw, or indentation strength method, it can be concluded that for these types of composite materials, the controlled flaw method of testing appears to result in more consistant critical stress intensity values at both RT and elevated temperature. This method requires less sample preparation than the SENB technique, and can easily be done at elevated temperatures and does not require microscopic measurement of crack length, thus having advantages over the indent technique. The notched or indent flawed RT flexural strengths of these composites were on the order of 35-50% of the un-notched strengths, compared to values of 78-90% found previously for either discontinuous or continuous NICALON fiber/LAS matrix composites. Thus, the whisker composites are significantly more notch sensitive than comparable NICALON fiber reinforced LAS matrix composites.

Although significant increases in both strength and toughness of glass-ceramics were found to occur by the incorporation of SiC whiskers, and that composite materials such as these could find application as high temperature structural components, especially as toughened matrices for continuous fiber composite, the environmental hazards of working with small diameter whiskers (hazards similar to that of asbestos) were deemed to be too great for the fabrication and handling facilities at UTRC. Although the proper environmental controls and safeguards have been employed at UTRC during the performance of this program, it was decided that the possible risks were greater than the rewards. Thus, the effort under this program was gradually shifted during the first quarter of 1990 to the study of fiber coatings for interface control in continuous fiber reinforced glass-ceramic matrix composites. Experiments dealing with the whisker composites already fabricated, such as the HRTEM of CAS matrix/Tokai SiC whisker composites, will be completed. However, the majority of the work since February, 1990, has dealt with coated fibers from a variety of sources. The results of the work to date on coated fibers and composites is detailed in Part II of this report.

PART I - WHISKER COMPOSITES

V. ACKNOWLEDGEMENTS

PART II - COATED FIBER REINFORCED GLASS-CERAMIC MATRIX COMPOSITES

I. INTRODUCTION

Fiber reinforced glasses and glass-ceramics have been under study at UTRC and other research organizations for a number of years as possible high temperature, lightweight, structural materials[35-50,69,77,78]. As stated earlier in Part I of this report, for the past few years this research at UTRC has concentrated on the study of the fiber/matrix interface and the relationship of the interfacial morphology, chemistry, and degree of bonding to the resultant composite mechanical and environmental properties[44,47,50]. From the results of these studies, it has been found that polymer derived Si-C-O or Si-C-N-O fibers such as NICALON, Tyranno (Ube Corp), and Dow Corning's MPDZ (methylpolydisilyla-zane), that contain excess carbon and oxygen over stoichiometric SiC, form a carbon rich fiber/matrix interfacial layer when incorporated into LAS glass-ceramic matrices at elevated temperatures. The exact mechanisms for the formation of this layer are not totally defined, but, as discussed earlier for carbon-rich SiC whiskers in LAS, may be related to diffusion of oxygen and silicon ions down the silica activity gradient that exists from fiber to matrix, as proposed by Cooper and Chyung[49]. The formation of this weak interfacial zone in these composites is responsible for the high toughness observed, in that it allows crack deflection to occur along the fiber/matrix interface and also allows load transfer from matrix to fiber to occur so that strengthening by traditional composite theory can take place.

Unfortunately, it has also been found that many of the weakly bonded, tough, and strong glass-ceramic matrix composites with either NICALON, Tyranno, or MPDZ fibers undergo an embrittlement and concurrent strength and toughness degradation when either stressed at elevated temperatures in an oxidizing environment or thermally aged in an unstressed condition for relatively long periods of time in an oxidative environment at temperature. In both cases, it appears that embrittlement occurs when the fiber/matrix interface is exposed to oxygen either through matrix microcracking under stress or from the "pipeline" oxidation of the carbon interfacial layer that initiates from cut ends of fibers that intersect the composite surface. The glassy oxide layer that then can form on the exposed fiber surfaces bonds the fibers tightly to the matrix, resulting in brittle composite behavior.

In the case of fibers that do not form an *in situ* carbon rich interface during glass-ceramic matrix composite processing, such as the high nitrogen HPZ (hydridopolysilylazane) fibers from Dow Corning, or oxide fibers such as the mullite based Nextel fibers from 3M or the alumina based FP and PRD-166 fibers from DuPont, the fiber/matrix interfacial bonding is strong, with resultant composite behavior that is weak and brittle. In the case of HPZ fibers, a reaction occurs during composite processing that forms silicon oxynitride at the fiber/matrix interface[50], similar to that seen for silicon nitride whiskers in LAS matrices, as discussed in Part I of this report. A large amount of fiber/matrix interdiffusion also occurs for the above systems, contributing to weakening of the fibers.

Thus, it is imperative that the fiber/matrix interface in the types of composites discussed above be controlled, or "engineered", so that relatively weak interfacial bonding exists for matrix crack deflection while maintaining oxidative stability. This can be accomplished in the carbon interfacial layer systems by doping the matrix such that the carbon layer becomes more resistant to oxidation. This approach is being studied at UTRC but suffers from the drawback of reducing the useful composite application temperature[79]. Another approach is through the use of fiber coatings that are applied to the fiber surfaces prior to composite fabrication. The purpose of these coatings is to weaken the interfacial bonding in those composite systems that bond too strongly for tough composite behavior to be achieved, or to improve the oxidation characteristics of those systems that suffer from oxidative instability at the fiber/matrix interface. In addition, in those systems where a reaction occurs between fiber and matrix, the fiber coating can act as a diffusion and reaction barrier. It is this approach; fiber coatings, that is being explored under the current AFOSR program.

PART II - COATED FIBER COMPOSITES

II. BACKGROUND

During the past few years, the interest in fiber coatings as a means of controlling the fiber/matrix interfacial properties in ceramic matrix composites has increased[50,68,80-86]. Most of these studies have dealt with composite systems that bonded too strongly to achieve tough composite behavior, but some have attempted to find a replacement coating for carbon that would debond like carbon but have improved oxidative stability. Studies conducted at UTRC in this area in the past few years have consisted of an investigation as a subcontractor to Dow Corning Corp. on a DARPA/AFML program to evaluate a variety of fiber coatings on NICALON and HPZ fibers[80], an ONR program studying the effect of coatings on monofilament boron and SiC fibers in glass matrices[82], as well as an ONR program to investigate BN coatings on NICALON fibers in a chemically vapor infiltrated (CVI) SiC matrix[83]. In addition, BN coatings on NICALON fibers for application in glass-ceramic matrices have been conducted under in-house programs at UTRC.

Under the Dow Corning subcontract, CVD coatings on NICALON fibers applied by either Battelle Labs, Columbus, OH, or American Cyanamid, Stamford, CT, included SiC, C, C over SiC, C over SiC over C, Al_2O_3, Si_3N_4, Nb, and Ir. For a variety of reasons, including dissolution into the LAS matrix (Al_2O_3, Si3N4), excessive reaction with the fibers during either CVD deposition (SiC) or composite processing (Nb, Ir), only the coatings containing carbon, with and without SiC overcoats, gave weakly bonded interfaces and acted as good diffusion barriers. Carbon coatings on HPZ fibers also resulted in weakly bonded interfaces and strong and tough LAS and BMAS (barium magnesium aluminosilicate) matrix composites. However, none of the coatings that contained pure or relatively pure carbon were stable at elevated temperatures in oxidizing environments, and thus were not practical as high temperatu. oxidation resistant interfaces.

In CVI SiC matrix/NICALON fiber composites, a layer of carbon is often utilized as a weakly bonded interface between the fibers and the matrix, with an overcoat of CVD SiC being applied to the finished composite for oxidation protection. However, if this CVD SiC overcoat is damaged due to overstress or impact, or simply careless handling, oxygen can permeate through the cracks in the coating, oxidize the interfacial carbon layer, and render the composite useless. In an ONR

program at UTRC[82], it was discovered that a layer of CVD BN applied to the NICALON fibers prior to infiltration of the CVI SiC matrix resulted in a composite with excellent strength and toughness, as well as good strength retention in oxidizing environments at temperatures up to 1200°C.

From in-house work conducted at UTRC, it was found that the use of BN coated NICALON fibers in a refractory LAS matrix resulted in a composite that exhibited excellent oxidative stability compared to the uncoated fiber composite and good strength at temperature in air to over 1100°C, as shown in Table VI. The BN coatings were applied at Synterials, Inc, Herndon, VA, and were not pure BN, as can be seen from the SAM depth profile of the as-received coated fibers (Fig. 32), but contained excess B, a rather high amount of oxygen, and slight Al impurity. Attempts to repeat and expand upon this experiment were not successful due to inconsistant BN fiber coatings and fiber breakage problems for subsequent lots of coated fiber obtained from Synterials. However, the fiber breakage problems that were encountered were most likely caused from certain lots of poor quality NICALON fiber produced by Nippon Carbon Co. in 1987 and 1988, and not as a result of the BN fiber coating process.

In mid-1989, General Atomics (GA), San Diego, CA, was awarded a DARPA contract, monitored by AFOSR, to investigate coatings for ceramic fibers to be utilized in ceramic, intermetallic, and metal matrix composites. A variety of fibers will be coated, including NICALON, HPZ, Nextel, FP, etc, with a wide variety of coatings that include BN, SiC, Si_3N_4, oxides (Y_2O_3, Al_2O_3), TiB_2, AlN, and refractory metals. Some of these coatings will be suitable only for metal or intermetallic matrix composites, while others will only be suitable for ceramic matrix composites. One of the goals of the restructured AFOSR program at UTRC will be to investigated the latter coatings from GA for applicability to glass-ceramic matrix composites.

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III. TECHNICAL DISCUSSION

The research under this program is divided into four main tasks: I. Coated Fiber Characterization; II. Glass-Ceramic Matrix/Coated Fiber Composite Fabrication; III. Microstructural and Microchemical Analysis of Composites; and IV. Composite Mechanical and Thermal Testing. These tasks are set up to run concurrently and are iterative with one another.

While the main source of coated fibers to be investigated under this program will be General Atomics, from their DARPA/AFOSR program, other coated fibers will also be investigated. The other sources for coated fibers will include UTRC, 3M, and possibly Union Carbide, as well as any other coated fiber that is deemed worthy of investigation under this program. To date, the coated fibers that have been received at UTRC under this progam include Y_2O_3 coated NICALON from GA, a series of BN coated NICALON from GA, BN coated NICALON produced in-house at UTRC, and BN and SiC over BN coated NICALON from 3M. Only the yttria and BN coated NICALON fibers from GA have been investigated sufficiently for inclusion in this report.

A. General Atomics Y_2O_3 Coated NICALON Fibers

Two different batches of yttria coated NICALON fibers were received from GA. These coatings are intended primarily for use in intermetallic matrix composites, but since they were available, it was decided to characterize them for coating chemistry and fiber strength and evaluate the reactivity of this coating in a glass-ceramic matrix. These coatings are applied to the NICALON fibers by a sol-gel process involving running the fibers through a yttrium nitrate solution, hydrolyzing in ammonia, and then calcining or firing the coated fibers to temperatures of 800-900°C in order to convert the coating to Y_2O_3. Figure 33 shows the fractured ends of lot #39066-127 yttria coated NICALON, which was dipped in the yttrium nitrate solution seven times and calcined at 800°C, while Fig. 34 shows the appearance of lot #YN-10339-7-3 coated fibers, which were dipped fewer times and thus have a thinner coating. The UTS of 20 coated fibers from each lot was measured at UTRC and found to be 1840 MPa (267 ksi) for the thinner coating and 1390 MPa (202 ksi) for the thicker coating. The application of the yttria coating thus appears to degrade

the tensile strength of NICALON fibers, which is originally on the order of 2400 MPa (350 ksi), with the degradation increasing as the coating thickness increases.

SAM analysis of the two yttria coated fiber lots was done, with the results of the lot #39066-127 coated fiber being presented in Fig. 35. The particular fiber analyzed exhibited a coating thickness of ~1000Å, with the first 500Å being relatively close to stoichiometric Y_2O_3, while the rest appeared to grade rather gradually from yttria to the NICALON fiber composition, indicating that some interdiffusion between coating and fiber may have occurred during the firing process. The lot #YN-10339-7-3 coated fibers exhibited a similar composition, except that the coating was thinner with the result that Si and C were detected all the way through the yttria coating.

A small LAS matrix composite was fabricated by hand layup of the lot #39066-127 coated fibers in a generally 0° fiber orientation. The as-pressed RT fracture surface of this composite, hot-pressed at 1350°C for 20 min. at 13.8 MPa (2 ksi) pressure, is shown in Fig. 36. From this figure, it can be seen that the fracture surface is quite fibrous in nature with a flexural strength of 614 MPa (89 ksi). Considering the as-received tensile strength of the fibers was only 1390 MPa (202 ksi), and that the fiber volume fraction in the composite was ~50%, this flexural strength is quite respectable.

A SAM depth profile analysis of a fiber surface and a matrix trough on the fracture surface of this composite was performed, with the combined interfacial SAM analysis presented in Fig. 37. It can be seen that the yttria coating has completely disappeared from the fiber surface, allowing the normal 100-200Å thick carbon layer to form at the fiber/matrix interface. This carbon layer is responsible for the fibrous fracture behavior of this composite, as was seen in Fig. 36. It is thus apparent that, like alumina and silicon nitride fiber coatings previously evaluated[80], the yttria coating has dissolved completely in the LAS matrix during composite processing, with diffusion so complete that no yttrium could be detected in the SAM analysis of the matrix. Yttria is therefore not a viable candidate for an interface engineered fiber coating for glass-ceramic matrix composites, and probably not for any ceramic matrix composite due to its likelyhood of bonding rather strongly to or reacting with ceramic matrices and fibers.

B. General Atomics BN Coated NICALON Fibers

A series of relatively short lengths (1-2 m) of BN coated NICALON fiber was received from GA in April, 1990. These coatings were applied by a CVD process

utilizing diborane (B$_2$H$_6$) plus ammonia (NH$_3$) at deposition temperatures ranging from 500° to 1000°C. The five different BN coated NICALON fiber lots were subjected to SAM analysis in order to determine coating chemistry and thickness. The results of these analyses are shown in Figs. 38-42.

As can be seen from Fig. 38, the lot #10193-74 coating, which was deposited at 500°C for 30 min, is quite uniform in composition through the coating thickness of ~10,000Å (1 μm), with very little carbon or oxygen impurity, except near the surface. The very low oxygen content of this sample is the lowest ever seen at UTRC from Auger analysis of a variety of BN CVD coatings from various sources. The coating morphology was very smooth in appearance. Tensile testing of this lot of coated fibers was not successful, however, due to excessive fiber breakage during handling, probably caused by the thick coating bridging fibers and thus sticking them together. These fibers have been subjected to humidity testing and are awaiting TEM analysis in order to determine if the BN coating is amorphous, which is likely, or crystalline in nature. The moisture sensitivity of BN is an issue, especially for amorphous material formed at low temperatures.

The #10193-69 lot, deposited at 800°C for 25 min, as shown in Fig. 39, also was quite smooth in surface appearance but was much thinner (~1000Å), with a very high carbon content (~20%) and moderate oxygen (~8%). Like most other BN coatings analyzed, except for crystalline Boralloy BN from Union Carbide synthesized at over 1700°C, it was also boron rich. Figure 40 shows another lot (#10193-75) of BN coated NICALON fiber where the deposition temperature was 800°C. This particular lot of coated fiber exhibited very few smooth fibers with most fibers having a very rough or bumpy appearance. The SAM analysis shown in Fig. 40 was taken from one of the smooth fibers shown, and shows that the BN coating contained a very large amount of oxygen (~25%), very low carbon (~2%), and considerable excess boron. The thickness of the coating analyzed was about 3000-5000Å with some interdiffusion apparent between fiber and coating. A nodule or "bump" on one of the fibers was analyzed after sputtering into it for 5000Å and was found to be very high in boron and oxygen, with moderate nitrogen and minor carbon. Apparently, an oxygen leak must have occurred during this run. Twenty of these fibers were tensile tested with an average UTS of 1880 MPa (272 ksi).

The last two BN coated fiber lots, #10193-76 and -77, as shown in Figs. 41 and 42, were deposited at a temperature of 1000°C for a time of 30 and 65 min, respectively. Both coatings were relatively similar in composition, but different in thickness, as would be expected. Both coatings were boron rich with significant

amounts of carbon near the coating surface (<1000Å) and significant amounts of oxygen (15-20%) in the bulk of the coating. Interestingly, in both coatings the amount of oxygen impurity went down as the carbon impurity went up. The thinner coating (Fig. 41) also exhibited a large increase in boron just as the deposition began. Both of these coated fiber lots exhibited a RT UTS of ~1800 MPA (262 ksi) and had quite smooth surfaces. The BN coated fiber lot #10193-77 was also exposed to 100% relative humidity testing and is awaiting subsequent SAM analysis, as well as TEM analysis in the as-received condition.

The difference in BN coating chemistry between the lots received from GA is quite puzzling. From past experience in-house at UTRC with BN coatings applied to various fibers at UTRC, Synterials, and Union Carbide, utilizing boron trichloride (BCl3) plus ammonia as precursors for BN, the higher the deposition temperature, the more stoichiometric the BN coating and the fewer the impurities. Since the GA coating deposited at 500°C appeared to be the closest to stoichiometric BN and exhibited very low impurity content, the mechanisms for BN deposition from diborane plus ammonia precursors may be very different. Additional larger samples of BN coated NICALON fiber cloth from GA, deposited at 550°, 650°, and 750°C, have recently arrived at UTRC and will be subjected to SAM analysis as well as being utilized for an LAS matrix composite.

The results discussed above for the GA BN coated NICALON fibers have been sent to GA for their evaluation. It is anticipated that the reasons for the differences in coating composition, morphology, and thickness, can be discovered from the analysis of run conditions and repetitions of certain runs. If the parameters of deposition can be controlled such that BN coatings similar in composition and thickness to the 500°C run shown in Fig. 38 can be deposited in continuous fashion on enough NICALON fiber to actually fabricate a large enough composite, mechanical property measurements and environmental stability testing shall be done.

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IV. CONCLUSIONS

From the results obtained to date on this subject, it is apparent that yttria fiber coatings are not viable for glass-ceramic matrix composites, and that BN coatings applied to NICALON fibers exhibit variable chemistry that must be quantified and controlled before large quatities of coated fiber can be made in a reproduceable manner so that composite fabrication and characterization can be accomplished.

BN appears from initial UTRC in-house studies to be a viable coating candidate and should be persued. Currently, a variety of BN coated NICALON fibers are being evaluated from General Atomics, as well as UTRC in-house BN coatings and coatings applied by 3M. In addition, 3M has supplied UTRC with two other coatings on NICALON fibers consisting of SiC over BN and a slightly carbon-rich SiC over an extremely thin BN coating. The characterization and analysis of these coatings is currently in progress. If promising, these types of coatings will be applied to fibers other than NICALON, such as HPZ and Nextel 480 or other oxide type fiber, and evaluated in glass-ceramic matrix composites.

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V. ACKNOWLEDGEMENTS

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43

Table I

Composite Systems of Interest

Matrices	Whiskers	Coatings
Glass-Ceramics:	Silicon Carbide:	Carbon
LAS-I	ARCO	BN
LAS-A	Tokai	
CAS	Tokai TWS-400	
	LANL	
Ceramics	AMI	
Al_2O_3	Unocal	
	Silicon Nitride:	
	UBE	
	SiC Platelets-AMI	

Table II

Properties of LAS-I Matrix/AMI SiC Platelet Composites
(30 vol% platelets)

Comp. No.	Platelet Size	Condition	Flex. Strength-ksi(MPa)			RT K_{IC}- MPam^{1/2}
			RT	800°C	1000°C	
144-89	-200 mesh	As-Pressed	14 (97)	-	-	1.89
		Ceramed	15 (103)	-	-	-
220-89	-325 mesh	As-Pressed	12 (83)	-	-	1.81
		Ceramed	14 (97)	-	-	-
LAS (Corning 9608)		Ceramed	15 (103)	-	<10 (69)	0.85

Table III

Properties of LAS-I Matrix/Carbon and BN Coated SiC Whisker Composites
(30 vol% whiskers)

Comp. No.	Whisker	Condition	Flex. Strength-ksi(MPa)			RT K$_{IC}$-MPam$^{1/2}$
			RT	800°C	1000°C	
718-88	Tokai TWS-400	As-Pressed	52(358)	-	-	3.82
		Ceramed	54(372)	52(358)	45(310)	4.06
308-89	Tokai TWS-400C	AP	40(276)	-	-	3.88
	(Carbon Coated)	Cer	42(290)	42(290)	-	3.90
		+550°C, O$_2$	40(276)	-	-	-
289-88	ARCO SC-9	AP	58(400)	-	-	4.73
		Cer	57(393)	58(400)	42(290)	4.44
335-89	ARCO (BN Coated)	AP	36(248)	-	-	3.39
		Cer	38(262)	31(214)	-	3.35
		+550°C, O$_2$	31(214)	-	-	-

Table IV

Properties of LAS-I and CAS Matrix/ Tokai SiC Whisker Composites
(30 vol% whiskers)

Comp. No.	Matrix	Condition	Flex. Strength-ksi(MPa)			RT K$_{IC}$-MPam$^{1/2}$
			RT	800°C	1000°C	
718-88	LAS-I	As-Pressed	52(358)	-	-	3.82
		Ceramed	54(372)	52(358)	45(310)	4.06
499-89	CAS	AP	40(276)	-	13(90)	5.05
		Cer (1200°C)	42(290)	-	20(138)	4.27

Table V

Fracture Toughness and Flexural Strength of LAS and CAS
Matrix/ Tokai TWS-400 SiC Whisker Composites
(30 vol% whiskers)

Comp. #	Matrix	Whisker Type	Measurement Technique	K_{IC}-MPam$^{1/2}$		σ-MPa (ksi)	
				RT	800°C	RT	800°C
646-89	LAS-A	Tokai TWS-400	Flex	-	-	327(47)	-
			SENB	3.98	3.68	150(22)	138(20)
			Controlled Flaw	3.93	3.72	115(17)	131(19)
			Indent	4.47	-	-	-
645-89	CAS	Tokai TWS-400	Flex	-	-	363(53)	-
			SENB	4.98	3.88	197(29)	164(24)
			Controlled Flaw	4.72	4.73	146(21)	150(22)
			Indent	5.09	-	-	-
644-89	CAS	Tokai TWS-400C (Carbon Coated)	Flex	-	-	408(59)	-
			SENB	4.52	3.56	176(26)	141(20)
			Controlled Flaw	4.58	4.56	144(21)	144(21)
			Indent	3.73	-	-	-

Table VI

Properties of LAS Matrix/NICALON Fiber Composites
With and Without BN Fiber Coatings (0/90°)

BN Coating	RT Flexural Strength - MPA/(ksi)					Elevated Temperature Flex Strength - MPa/(ksi)				
	AP	Cer	After 70 hrs. O_2, T =			800°C	900°C	1000°C	1100°C	1200°C
			550°	700°	850°					
No	449 (65)	400 (58)	186 (27)	193 (28)	214 (31)	283 (41)	-	318 (46)	-	-
Yes	517 (75)	503 (73)	483 (70)	524 (76)	442 (64)	462 (67)	497 (72)	531 (77)	449 (65)	325 (47)

Fig. 1 American Matrix SiC Platelets (-200 Mesh)

Fig. 2 American Matrix SiC Platelets (-325 Mesh)
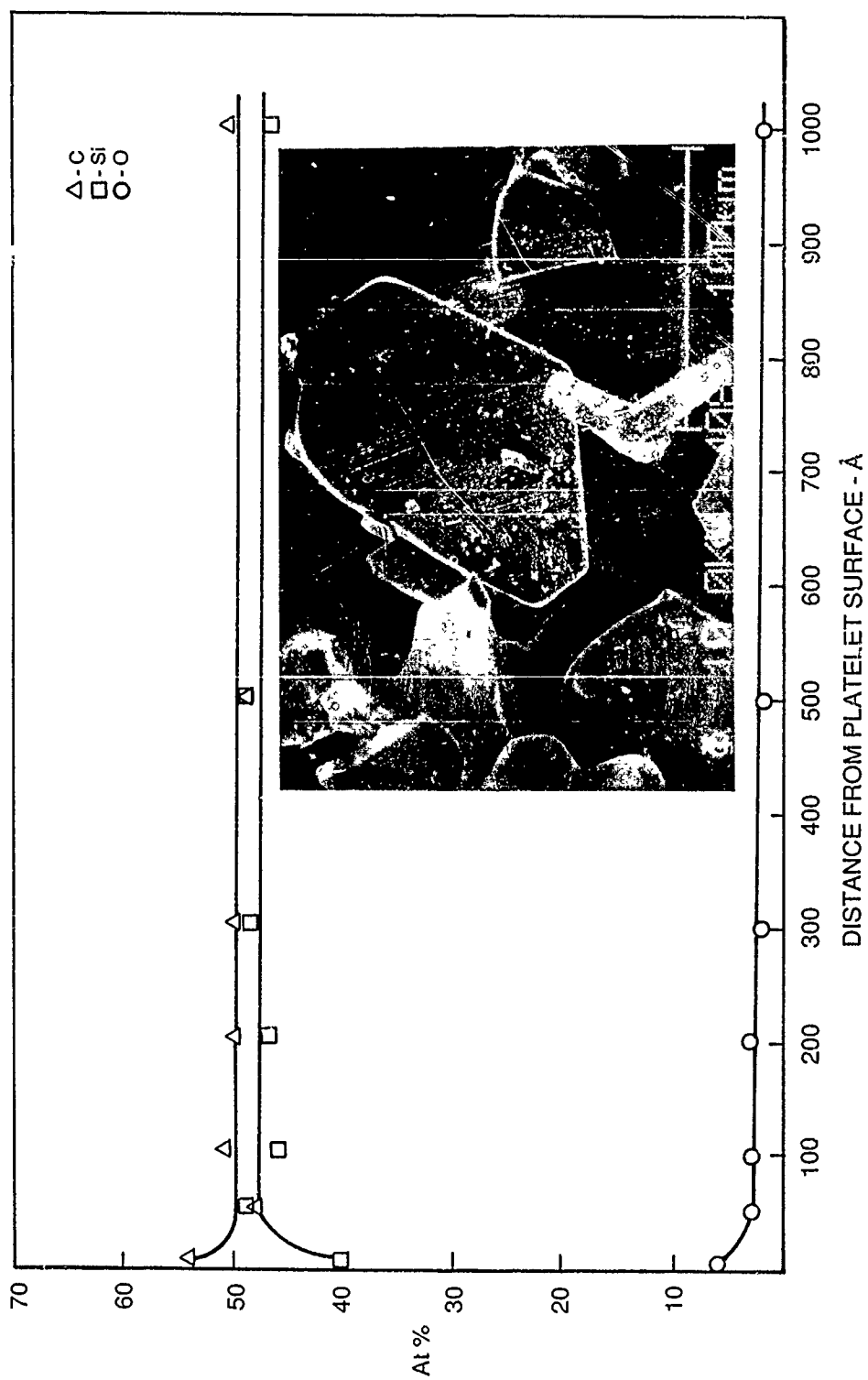
Fig. 3 SAM Depth Profile — American Matrix SiC Platelets (-325 Mesh) - As-Received

DISTANCE FROM PLATELET SURFACE - Å

At %

Δ - C
□ - Si
O - O
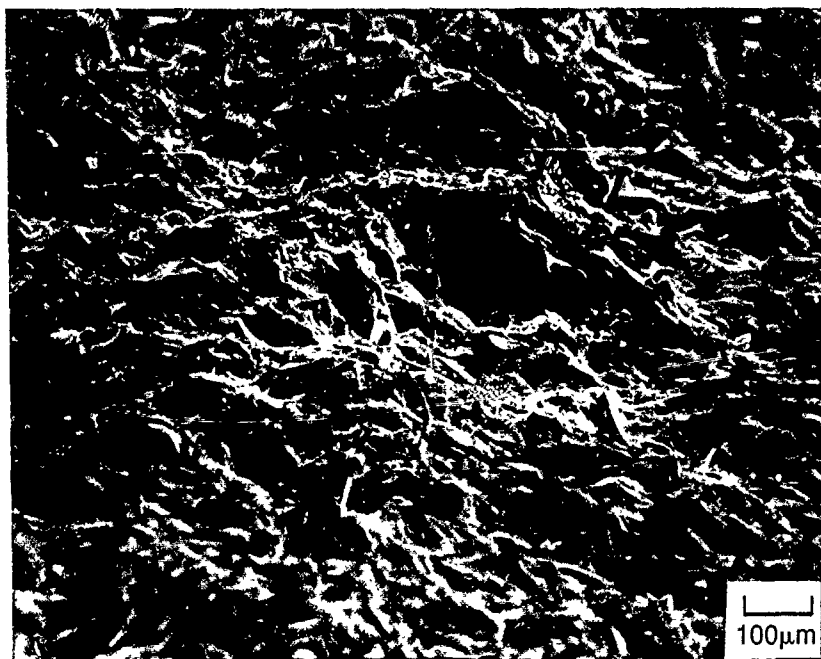
Fig. 4 Fracture Surface of LAS Matrix/SiC Platelet (-200 Mesh) Composite (#144-89)

B. AFTER 1000Å SPUTTER

A. AS-FRACTURED

DISTANCE FROM PLATELET SURFACE - Å

△ - C
□ - Si
○ - O

At %
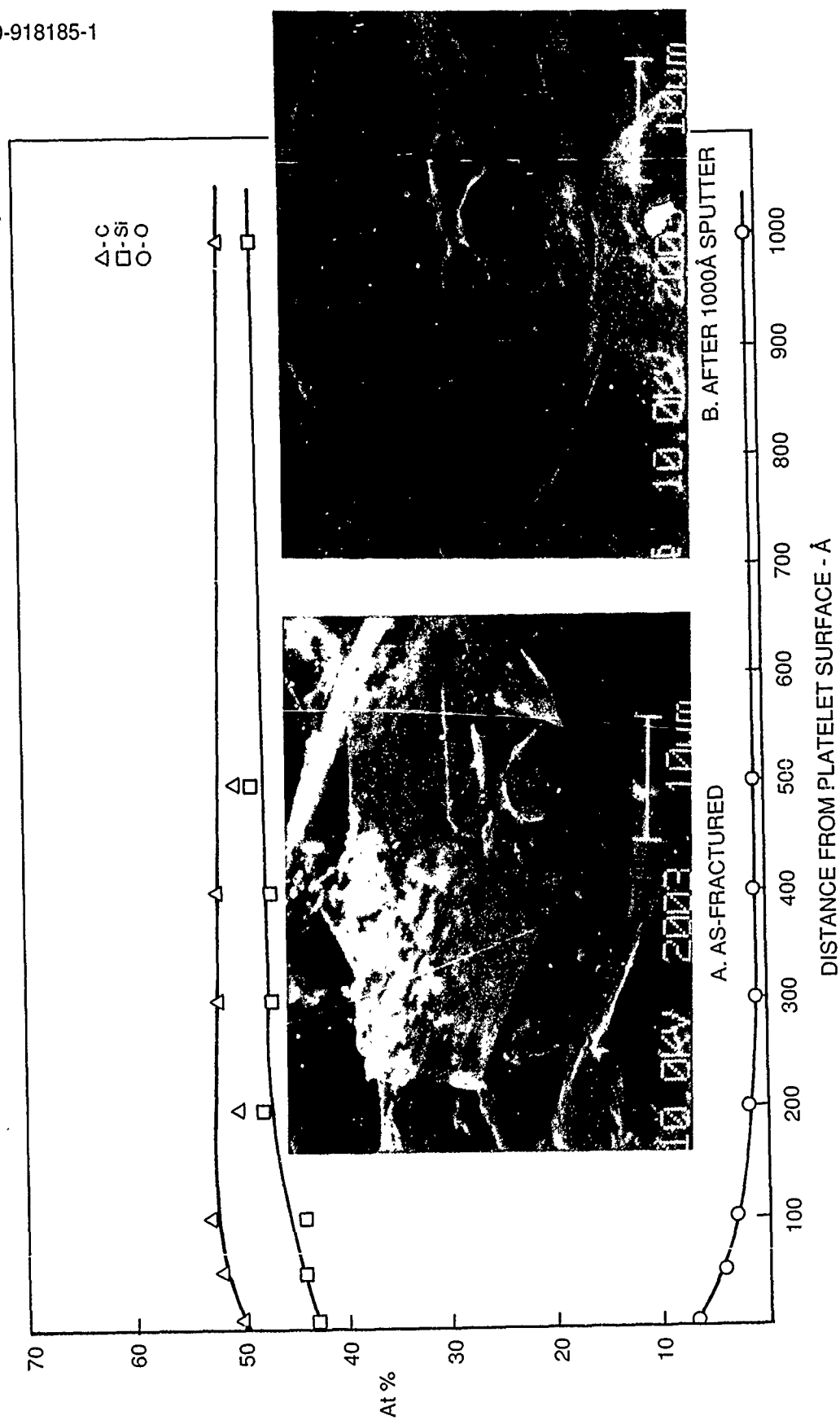
Fig. 5 SAM Depth Profile — LAS-I Matrix/SiC Platelet Composite #220-89 (Platelet Surface)

90-6-16-5
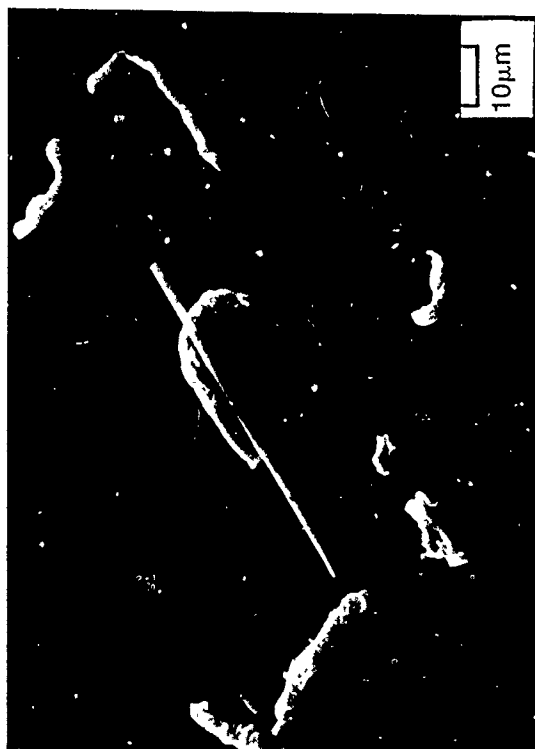
Fig. 6 Unocal SiC Whiskers (Lot N88)
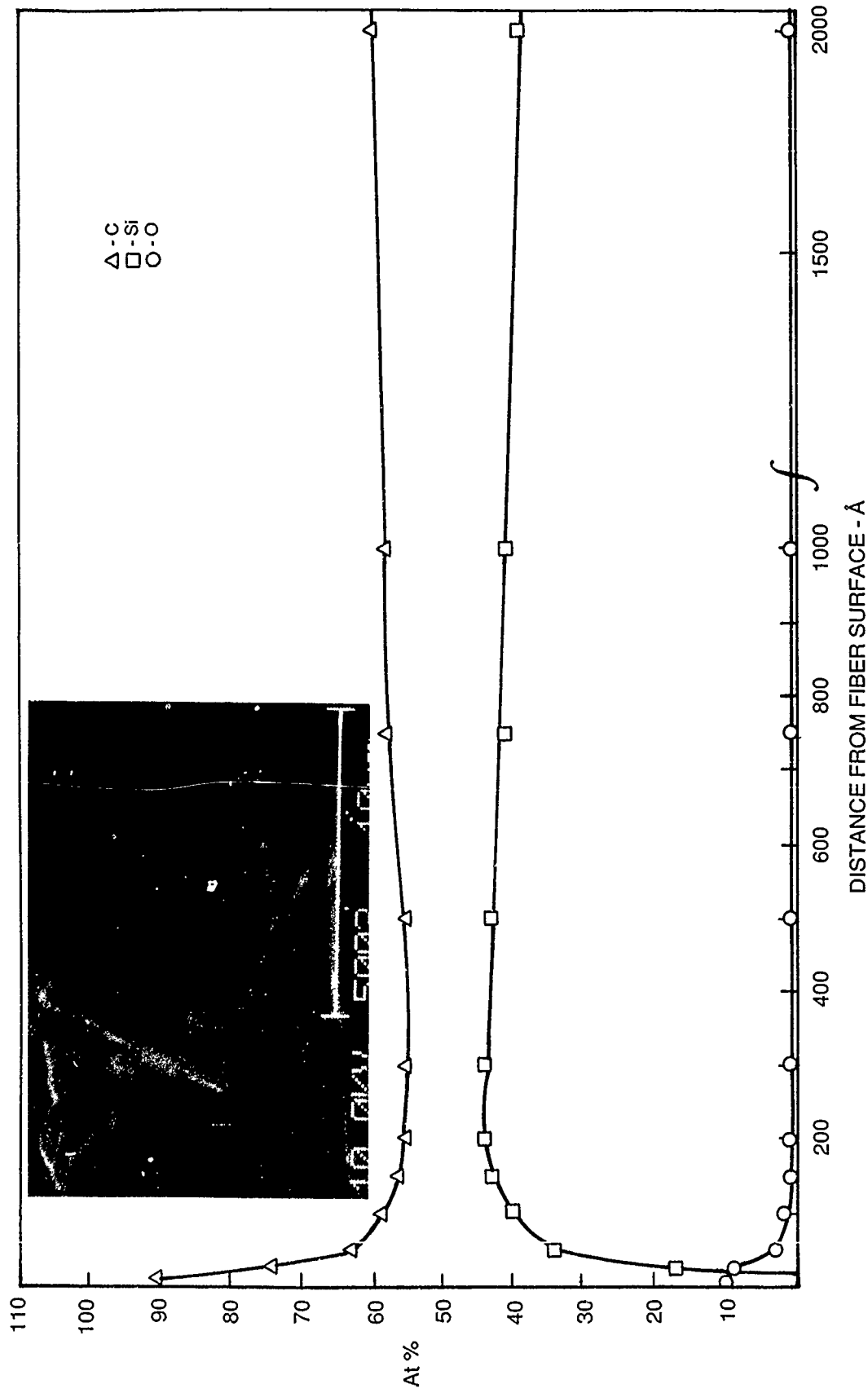
Fig. 7 SAM Depth Profile — Tokai TWS-400C SiC Whiskers (Carbon Coated)

90-6-16-7

Fig. 8 Fracture Surface of LAS-I Matrix/Tokai TWS-400C Carbon Coated SiC Whisker Composite #309-89

Fig. 9 Crack Growth Patterns in LAS-I Matrix/Tokai TWS-400C Carbon Coated SiC
Whisker Composite #309-89
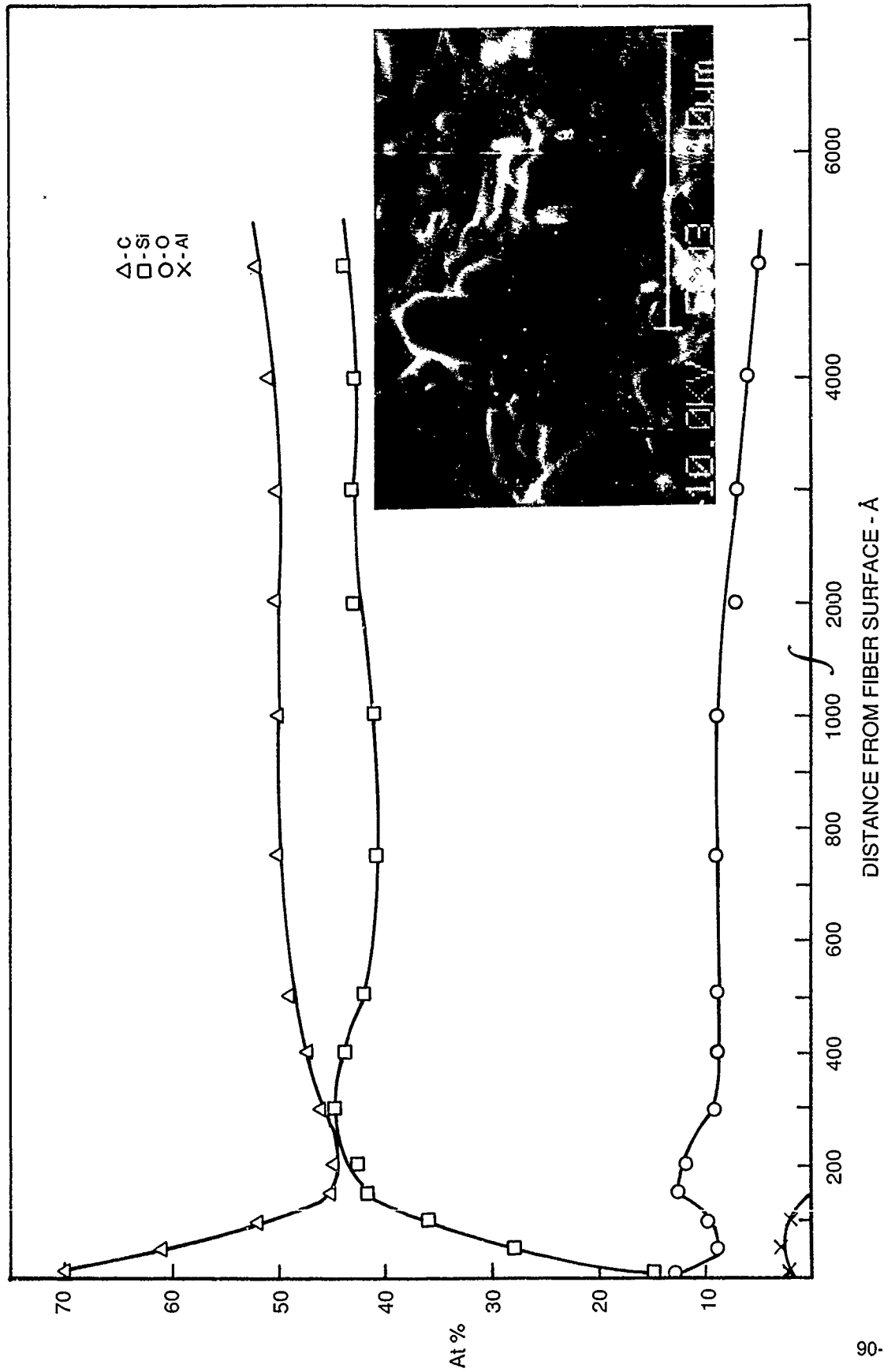
Fig. 10 SAM Depth Profile — LAS-I Matrix/Carbon Coated Tokai TWS-400C SiC Whisker Composite #308-89 (Whisker Surface)

90-6-16-10

AMORPHOUS MATRIX
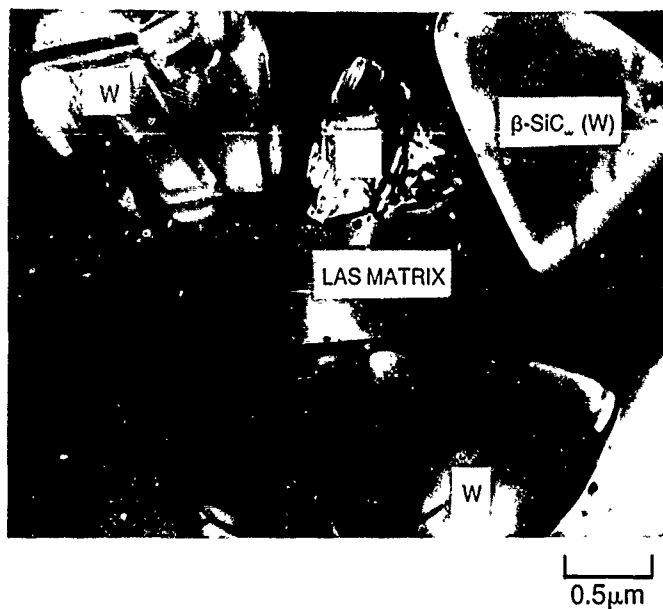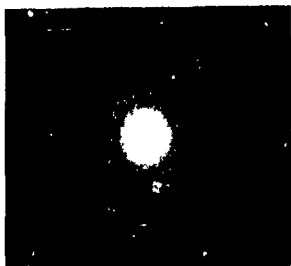
β-SiC WHISKER [110]$_{FCC}$
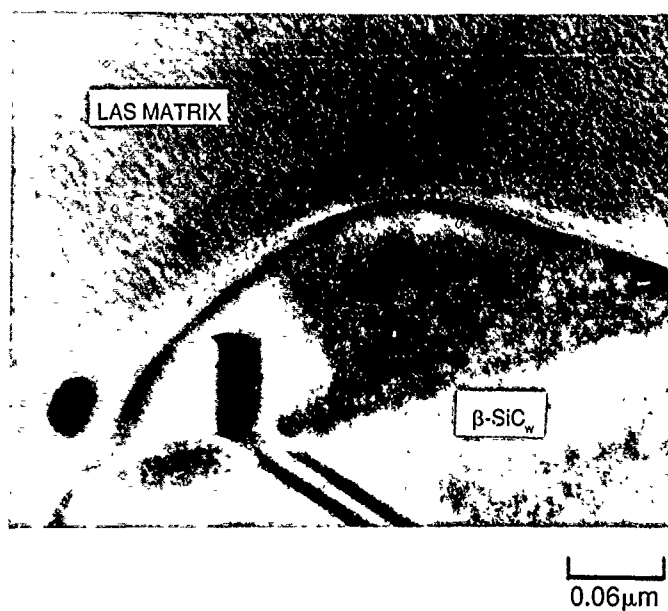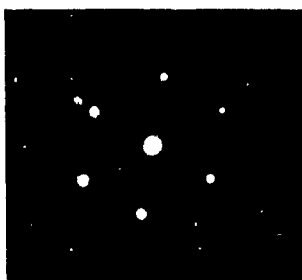
Fig. 11 TEM Thin Foil Characterization of LAS-I Matrix/Carbon Coated Tokai TWS-400C SiC Whisker Composite #308-89 (As-Pressed)

90-6-16-11

SURFACE OF WHISKER BUNDLE

LOOSE WHISKERS

AGGLOMERATED WHISKER BUNDLES

UNCOATED WHISKERS FROM BUNDLE INTERIOR
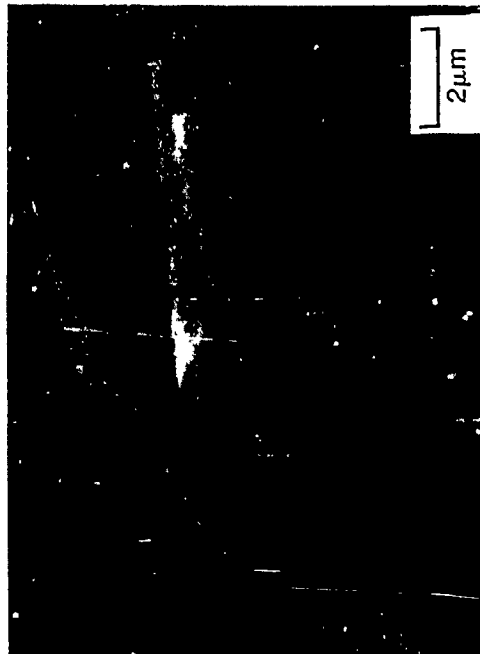
Fig. 12 Synterials BN Coated Arco SiC Whiskers (Lot 89-5-5)
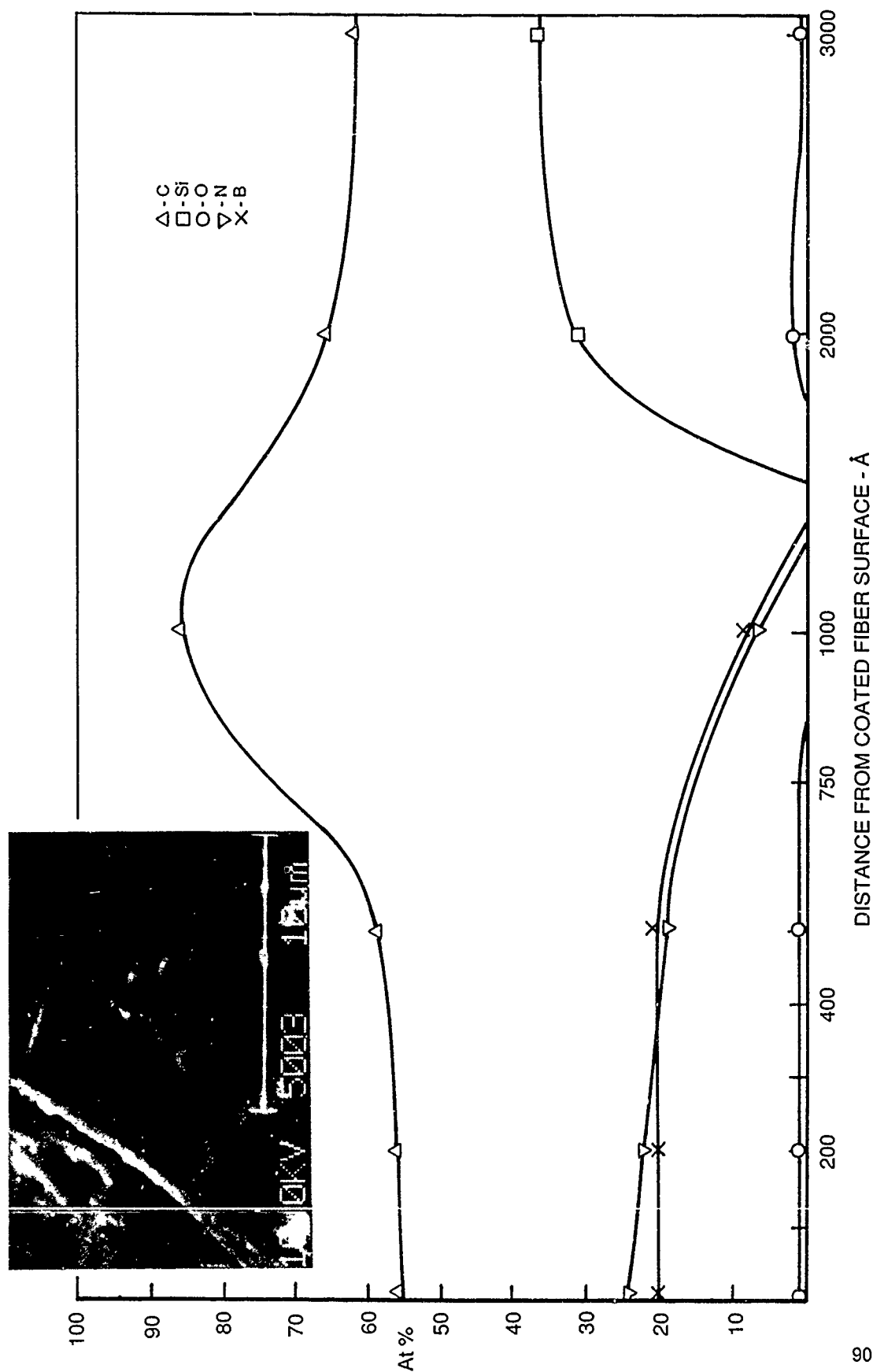
Fig. 13 SAM Depth Profile — Synterials CVD BN Coated Arco SiC Whiskers, #89-5-5

DISTANCE FROM COATED FIBER SURFACE - Å

At %

△ - C
□ - Si
○ - O
▷ - N
✕ - B

90-6-16-13
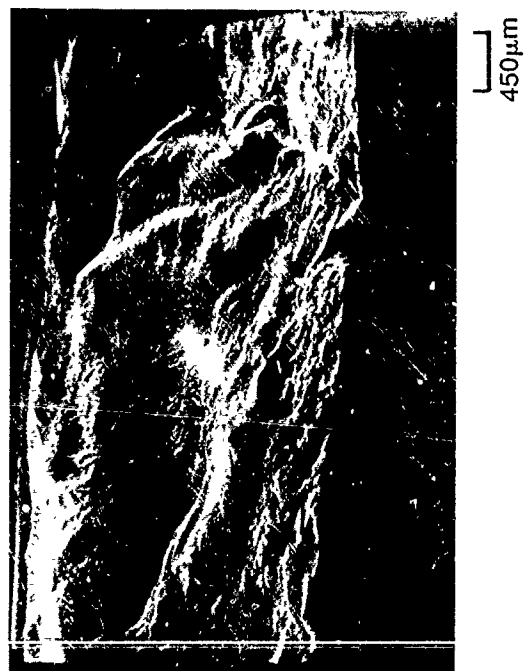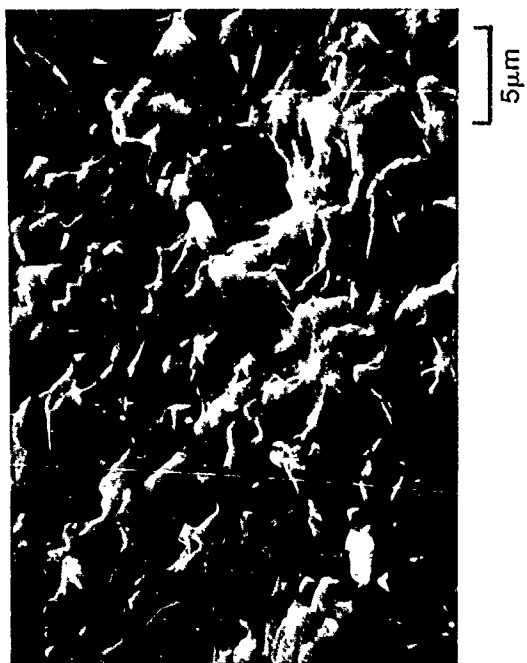
Fig. 14 Fracture Surface of LAS-I Matrix/BN Coated Arco SiC Whisker Composite #335-89

2μm

2μm
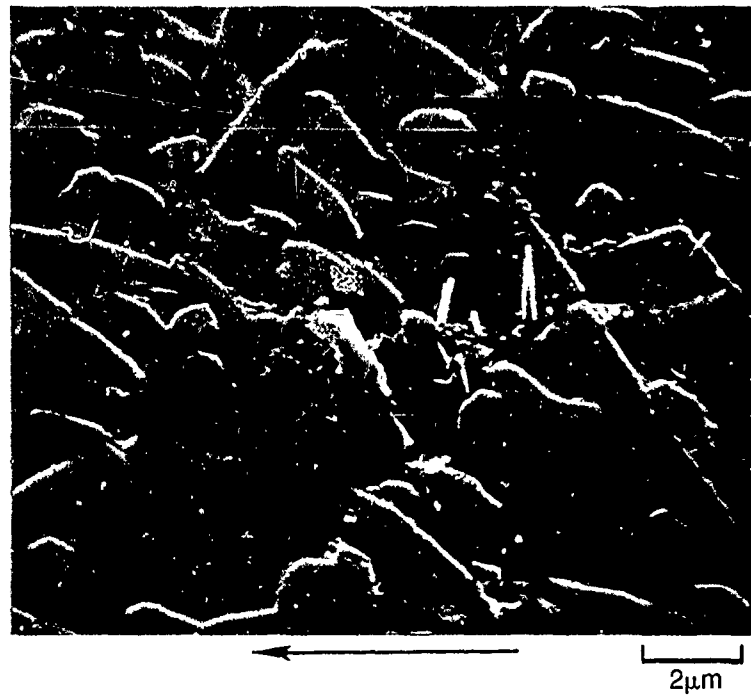
Fig. 15 Crack Growth Patterns in LAS-I Matrix/BN Coated Arco SiC Whisker Composite #335-89 (As-Pressed)
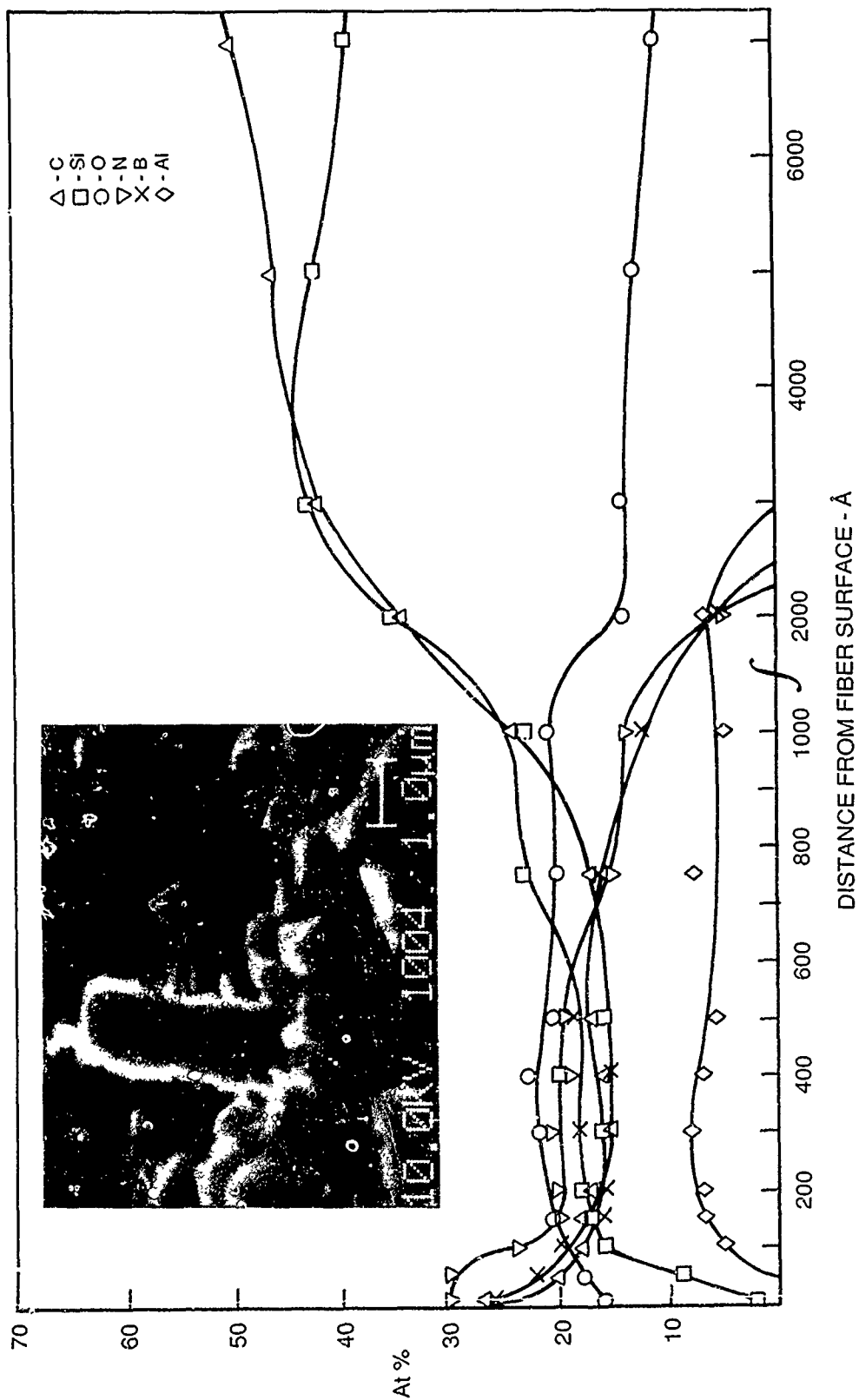
Fig. 16 SAM Depth Profile — LAS-I Matrix/BN Coated Arco SiC Whisker Composite #335-89
(Whisker Surface)

90-6-16-16
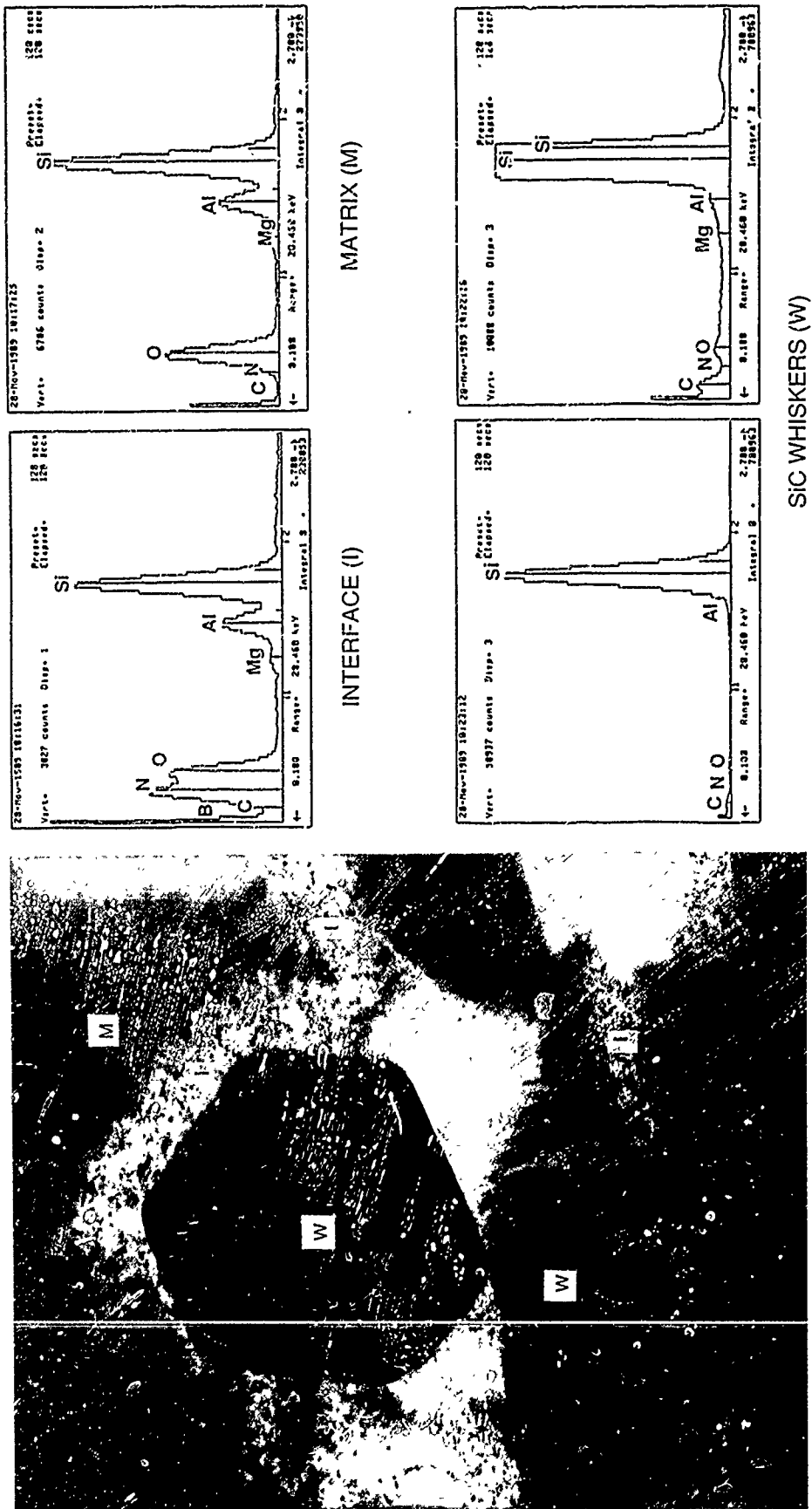
Fig. 17 TEM Thin Foil Characterization of LAS-I Matrix/BN Coated Arco SiC Whisker
Composite #335-89 (As-Pressed)

Fig. 18 TEM Thin Foil Characterization of LAS-I Matrix/UBE Si_3N_4 Whisker Composite #360-87 (As-Pressed)
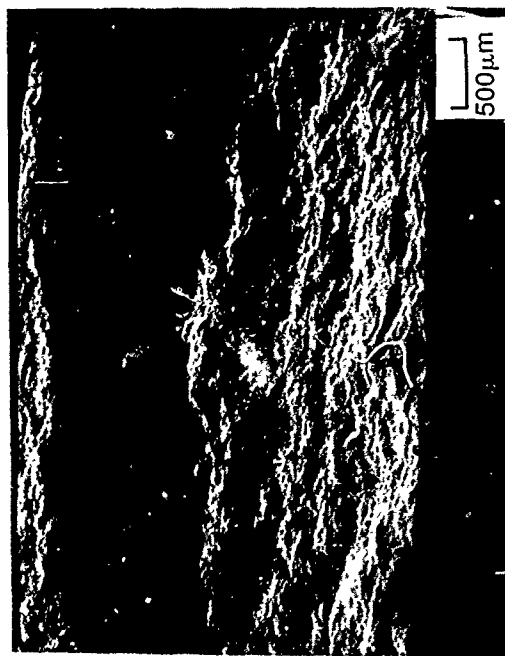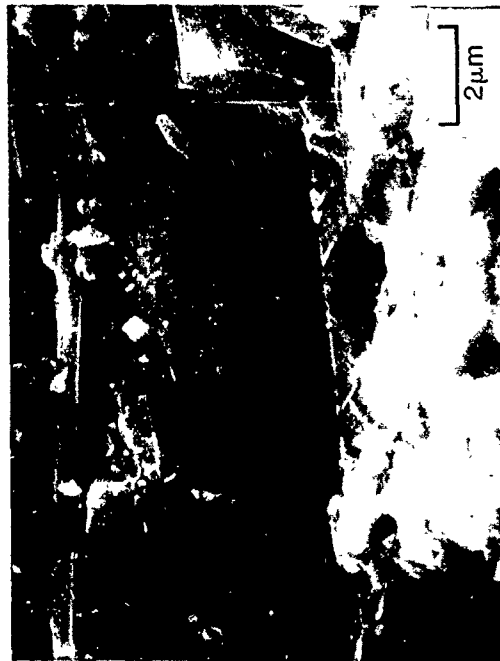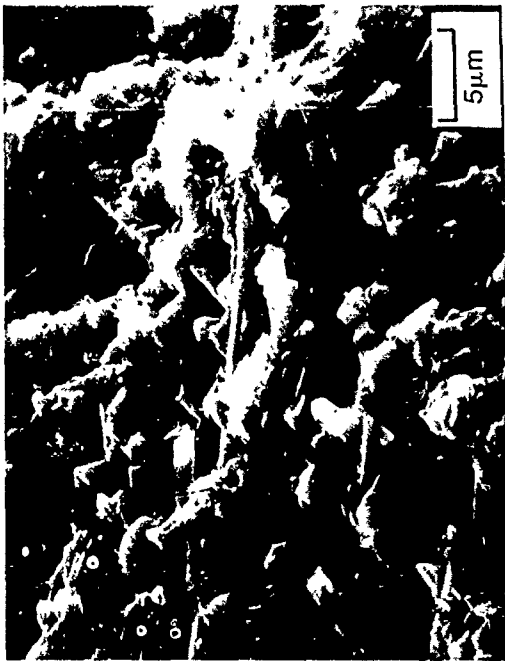
Fig. 19 Fracture Surface of CAS Matrix/Tokai TWS-400 SiC Whisker Composite #499-89
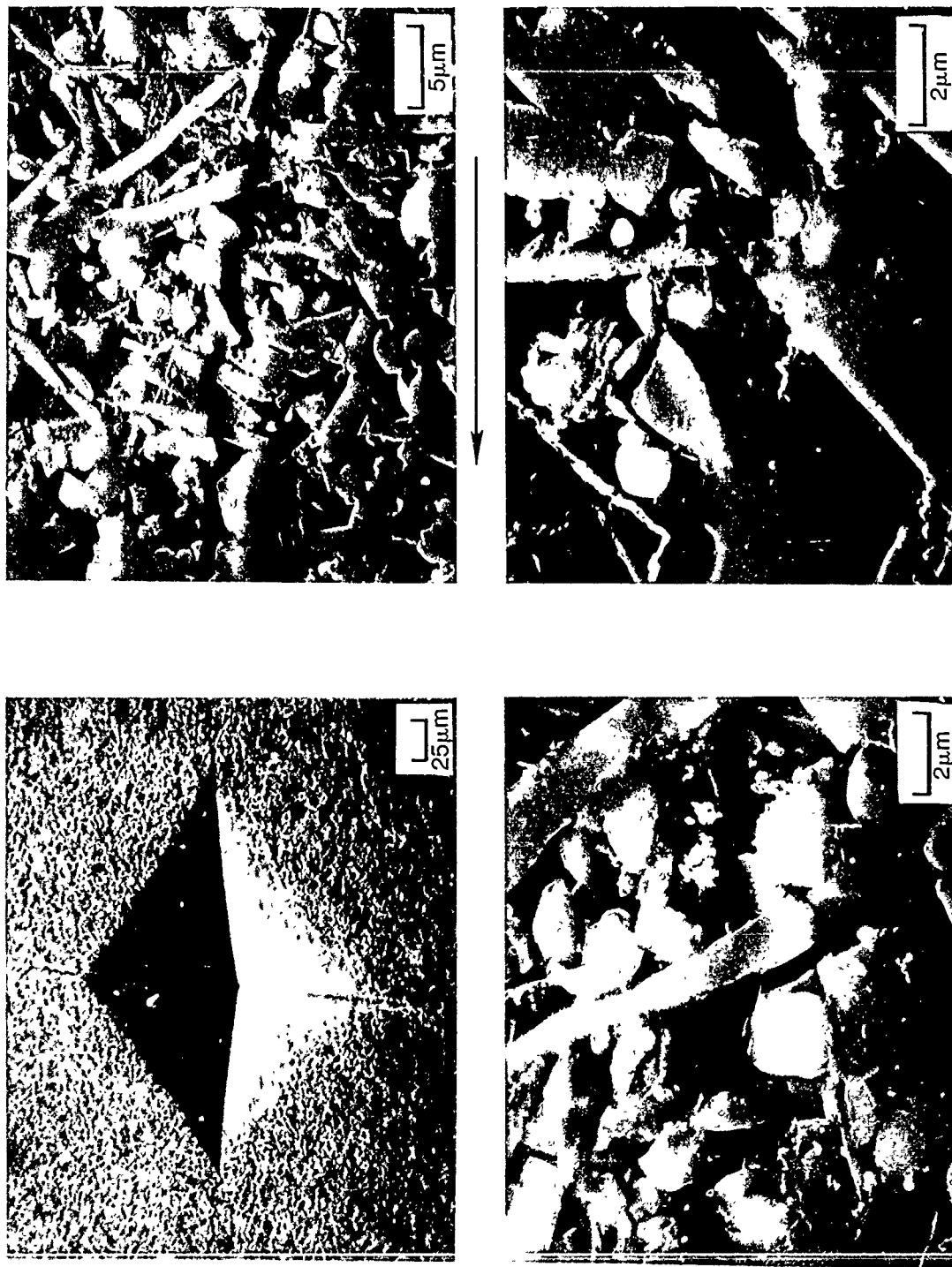
Fig. 20 Crack Growth Patterns in CAS Matrix/Tokai TWS-400 SiC Whisker Composite #499-89 (As-Pressed)
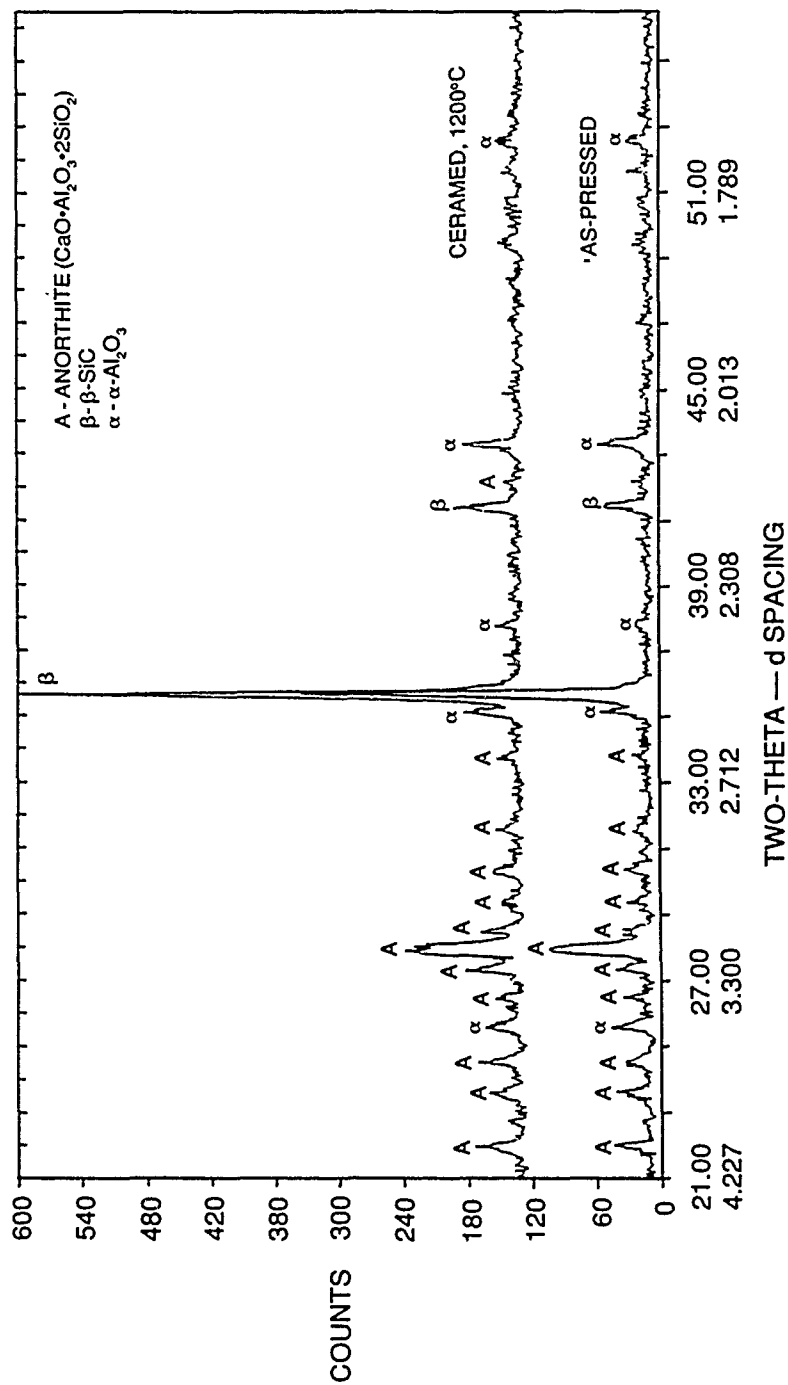
Fig. 21 X-ray Diffraction Analyses for CAS Matrix/Tokai TWS-400 SiC Whisker
Composite #499-69

Fig. 22 TEM Replica Characterization of CAS Matrix/Tokai TWS-400 — SiC Whisker Composite #499-89 (As-Pressed)
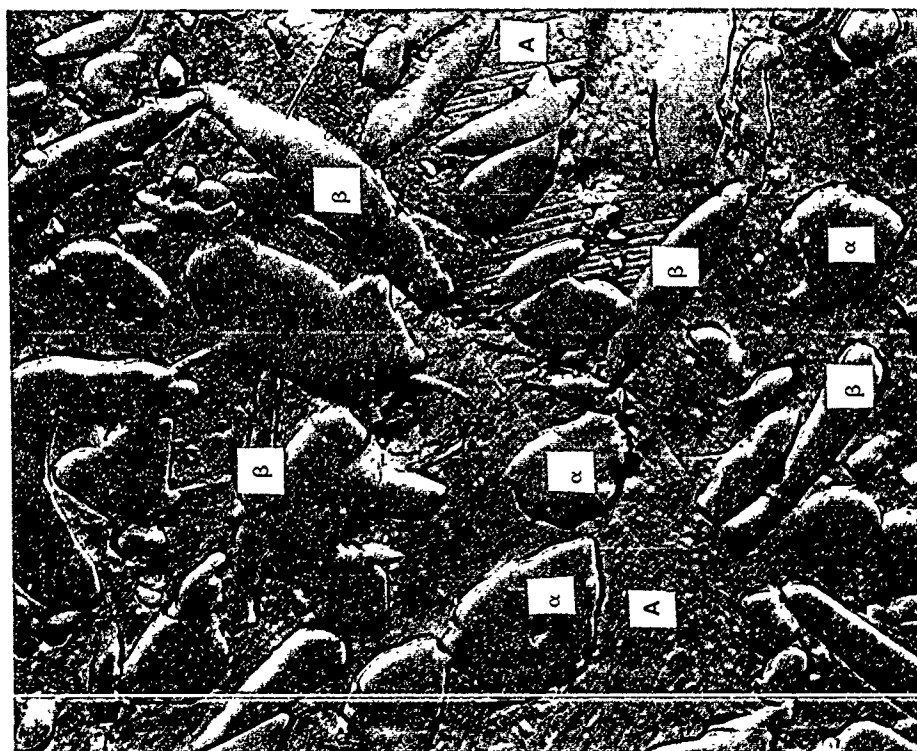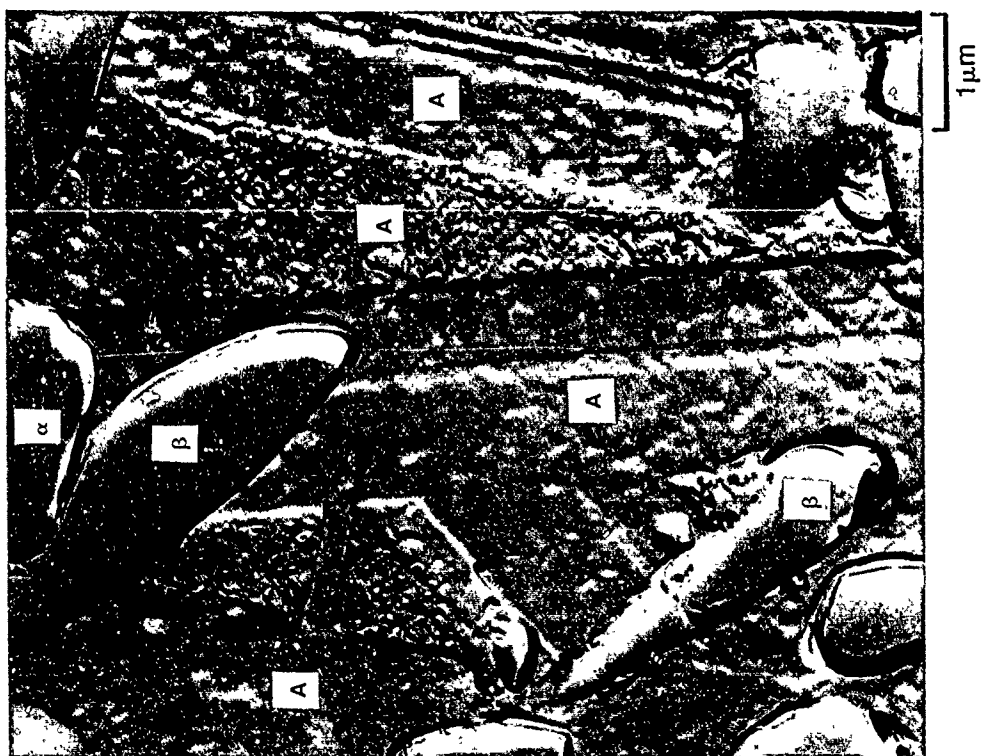
A - ANORTHITE
β - β-SiC$_w$
α - α-Al$_2$O$_3$

90-6-16-22
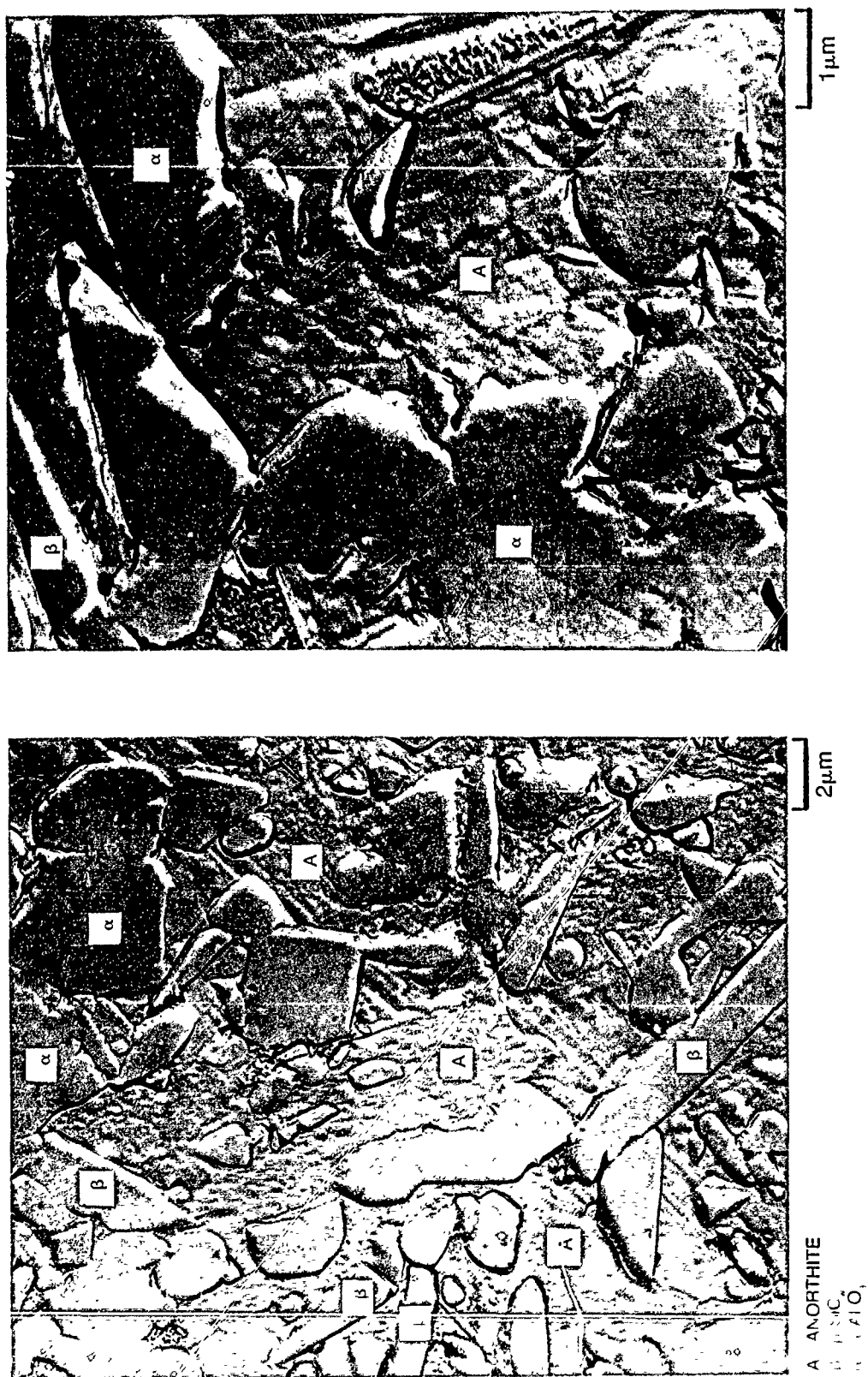
Fig. 23 TEM Replica Characterization of CAS Matrix/Tokai TWS-400 SiC Whisker Composite #499-89 (Ceramed, 1200°C)

A ANORTHITE

90-6-16-23

α – Al₂O₃ (α)

ANORTHITE (A)
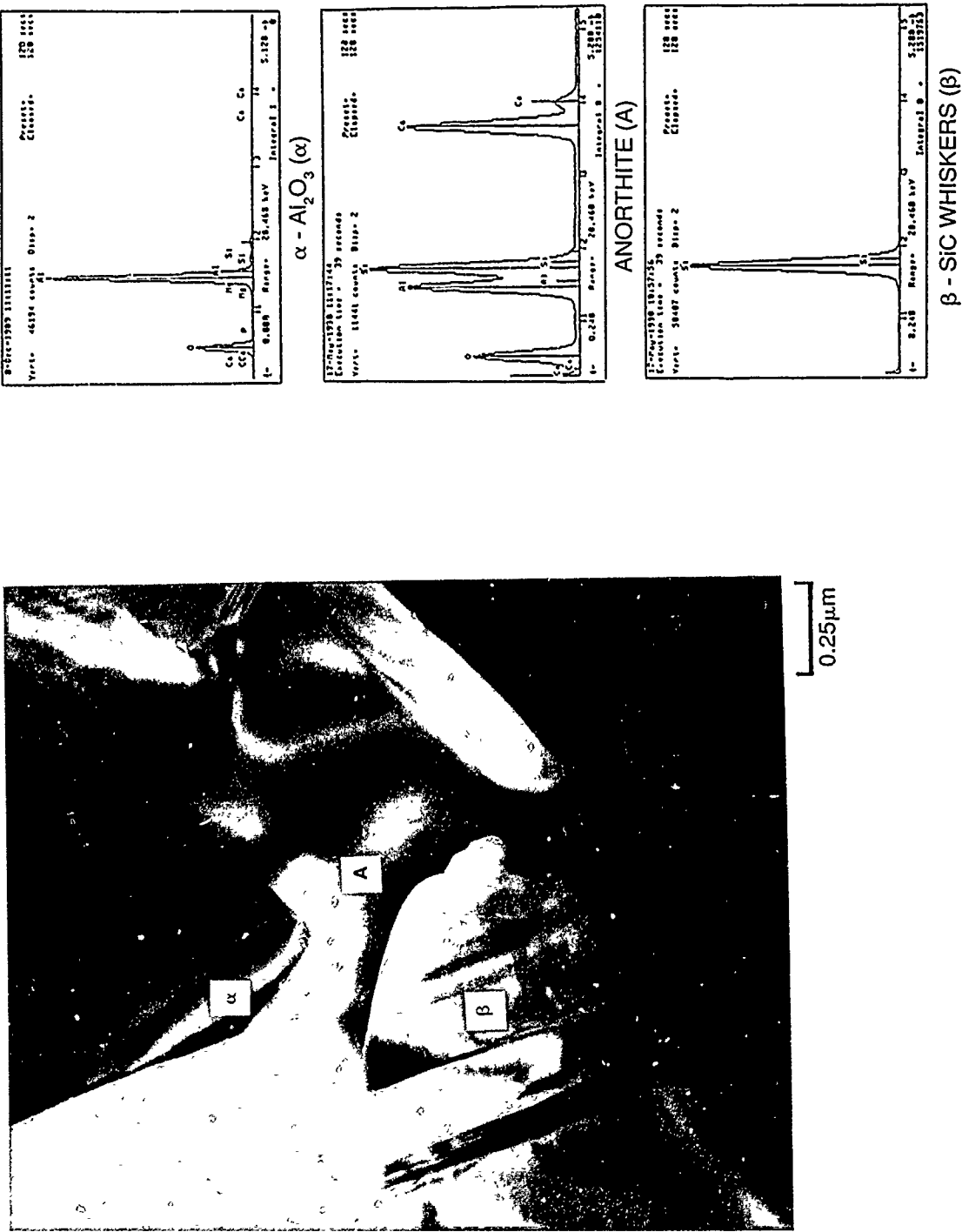
β - SiC WHISKERS (β)

Fig. 24 TEM/EDX Thin Foil Characterization of CAS Matrix/Tokai TWS-400 SiC Whisker
Composite #499-89 (As-Pressed)

0.25µm

α - Al$_2$O$_3$ (α)

CAS MATRIX (A)
(ANORTHITE)
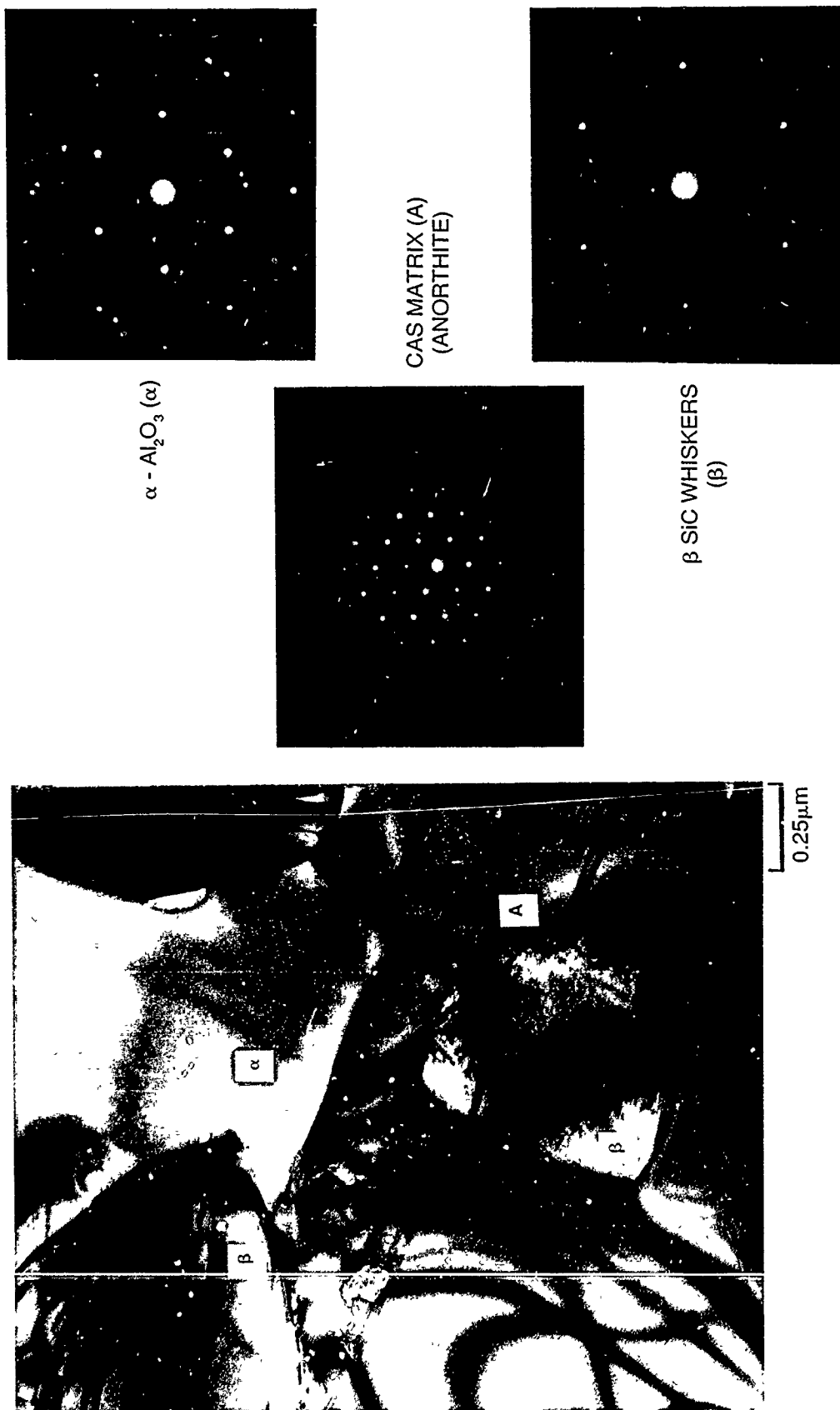
β SiC WHISKERS
(β)

Fig. 25 TEM/SAED Thin Foil Characterization of CAS Matrix/Tokai TWS-400 SiC Whisker
Composite #499-89 (As-Pressed)

0.25μm
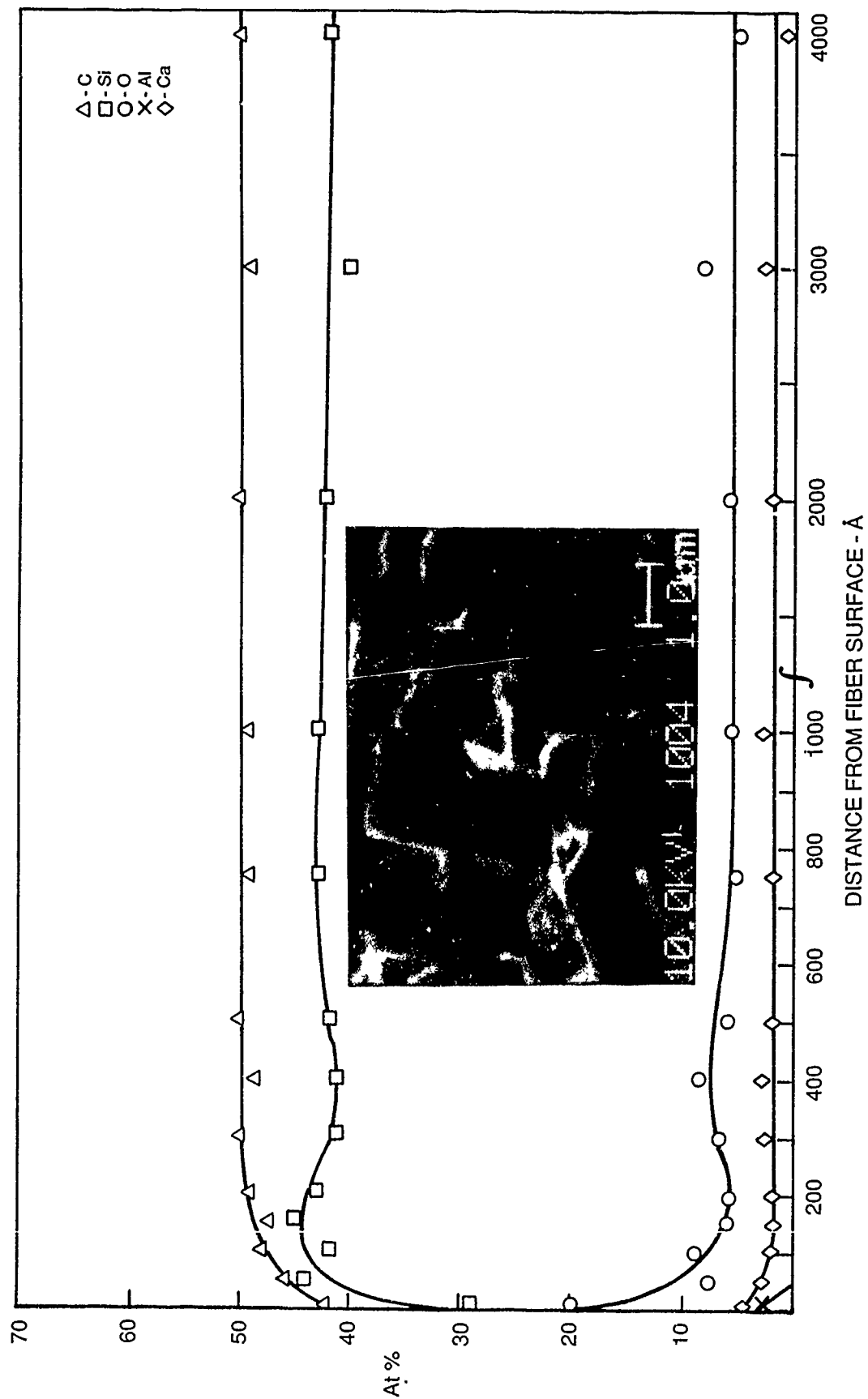
Fig. 26 SAM Depth Profile — CAS Matrix/Tokai TWS-400 SiC Whisker Composite #499-89 (Whisker Surface)

90-6-16-26
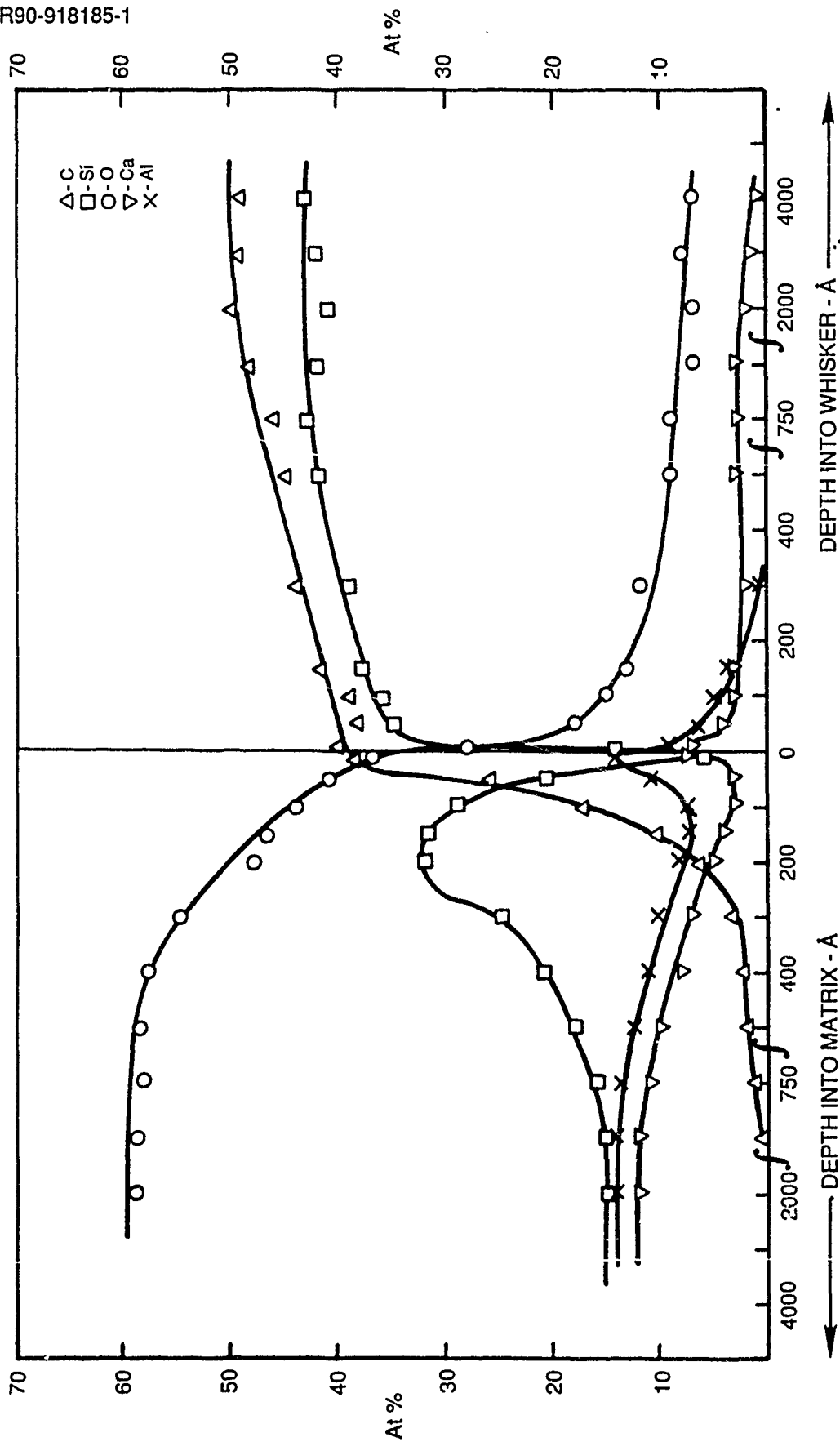
Fig. 27 SAM Depth Profile — Interfacial Chemistry of CAS Matrix/Tokai TWS-400 SiC
Whisker Composite #499-89 (Analysis #2)

90-6-16-27

Fig. 28 HRTEM Characterization of LAS-I Matrix/Tokai SiC
Whisker Composite #290-88

B.

A.
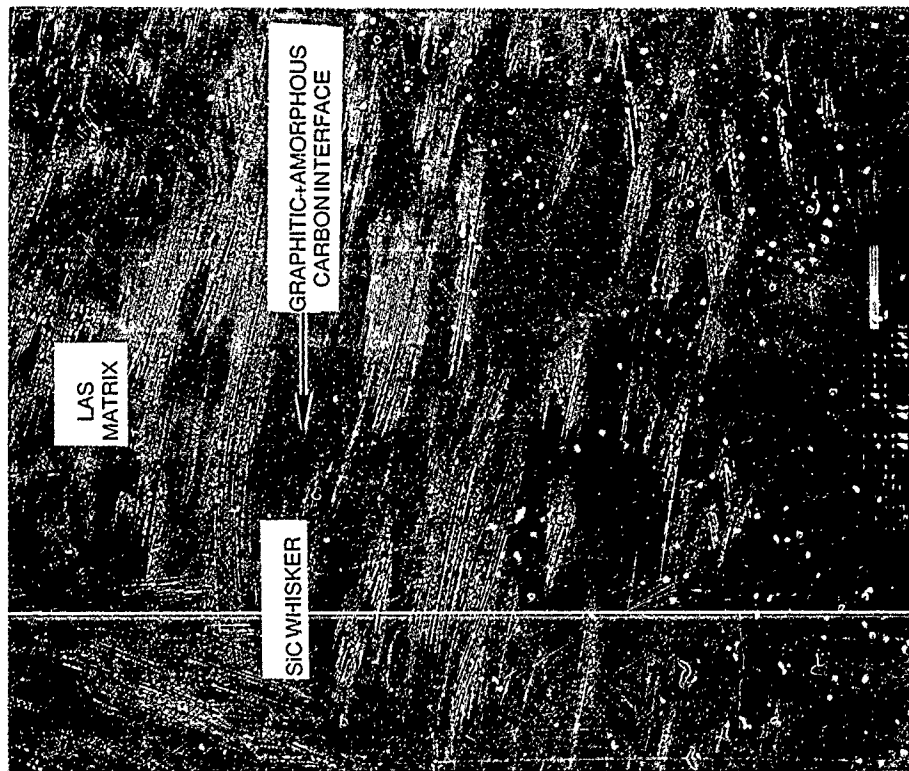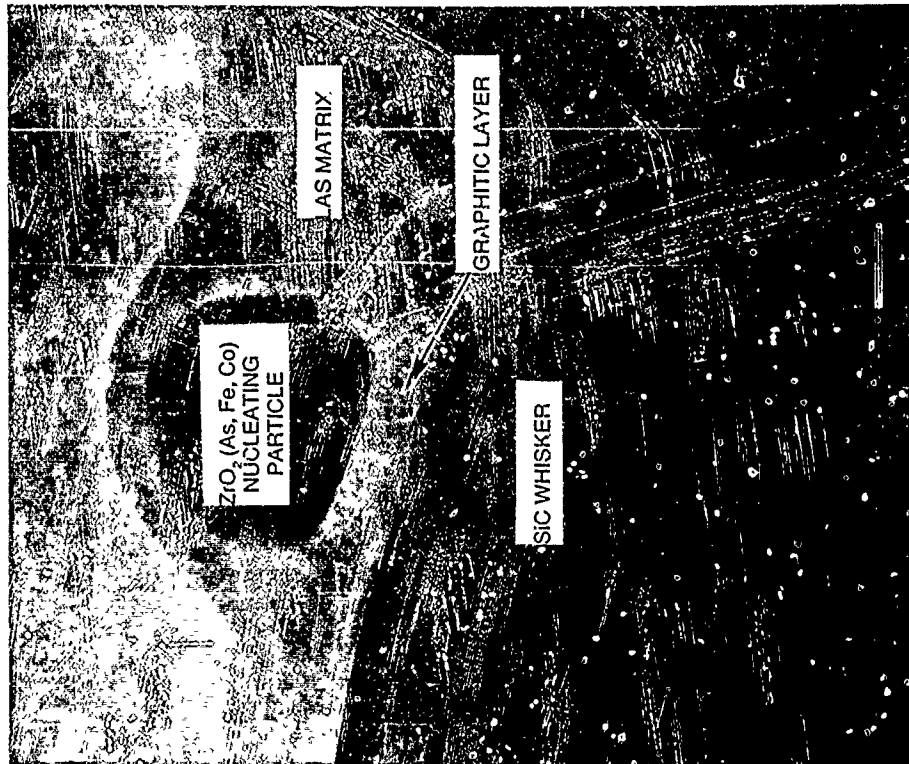
Fig. 29 HRTEM Characterization of LAS-I Matrix/Carbon Coated Tokai TWS-400C SiC Whisker Composite #308-89
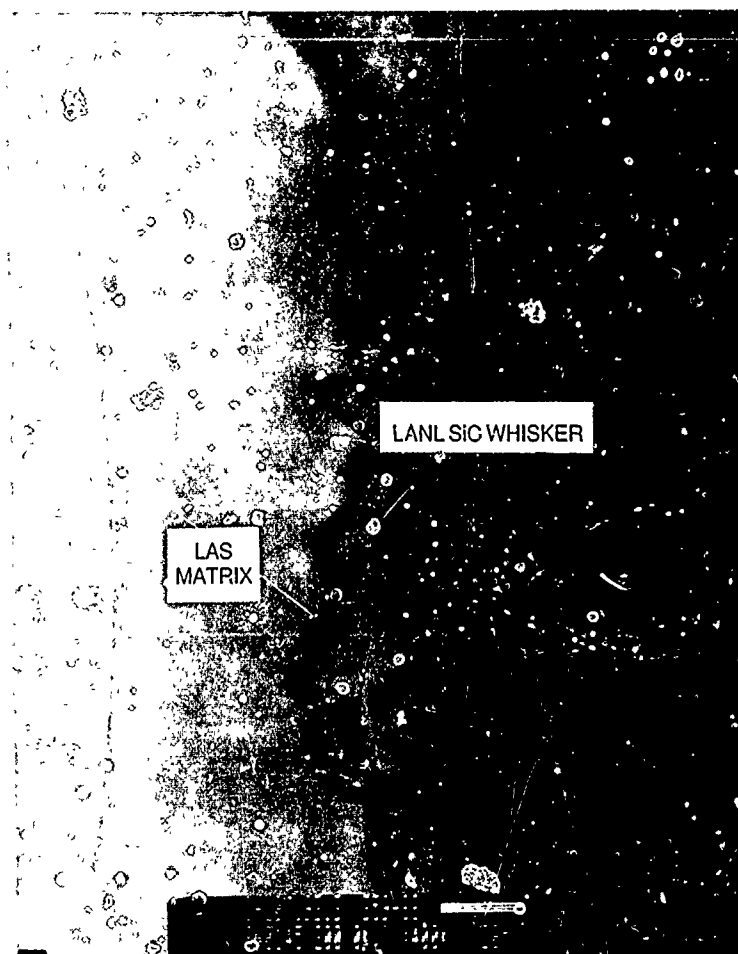
Fig. 30 HRTEM Characterization of LAS-I Matrix/LANL SiC
Whisker Composite #359-88

150μm
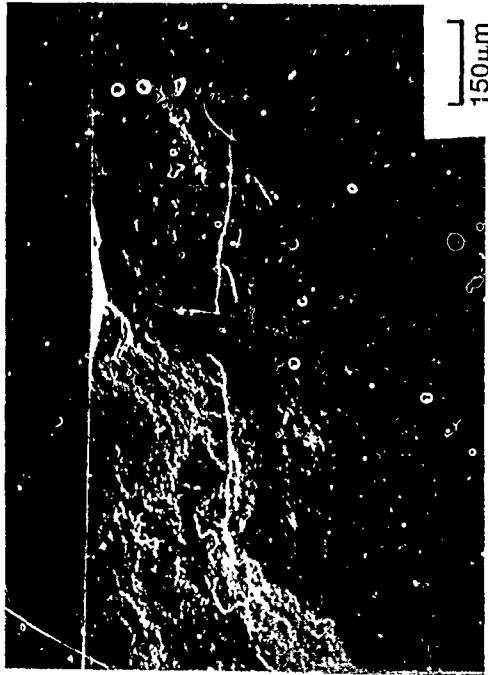
B) CONTROLLED FLAW (65 kg) - K_{ic} =3.93 MPa$\sqrt{m}$

417μm

A) SENB - K_{ic}=3.98 MPa$\sqrt{m}$
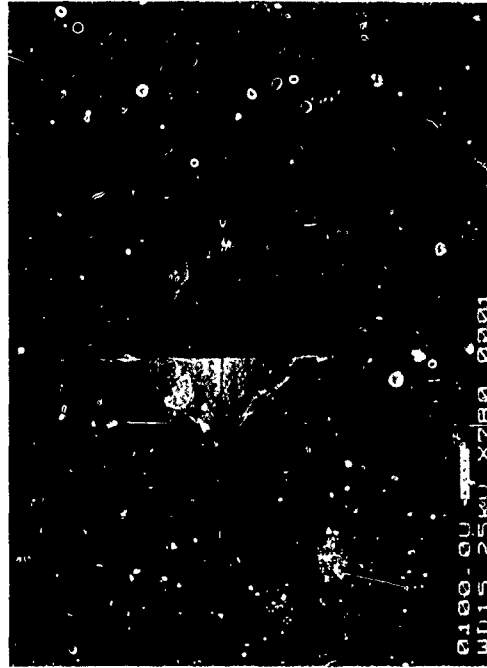
C) INDENT (100 kg) - K_{ic}=4.47 MPa$\sqrt{m}$

Fig. 31 LAS Matrix/Tokai TWS-400 SiC Whisker Composite #646-89 RT Fracture Toughness (K_{ic}) Samples (As-Pressed)
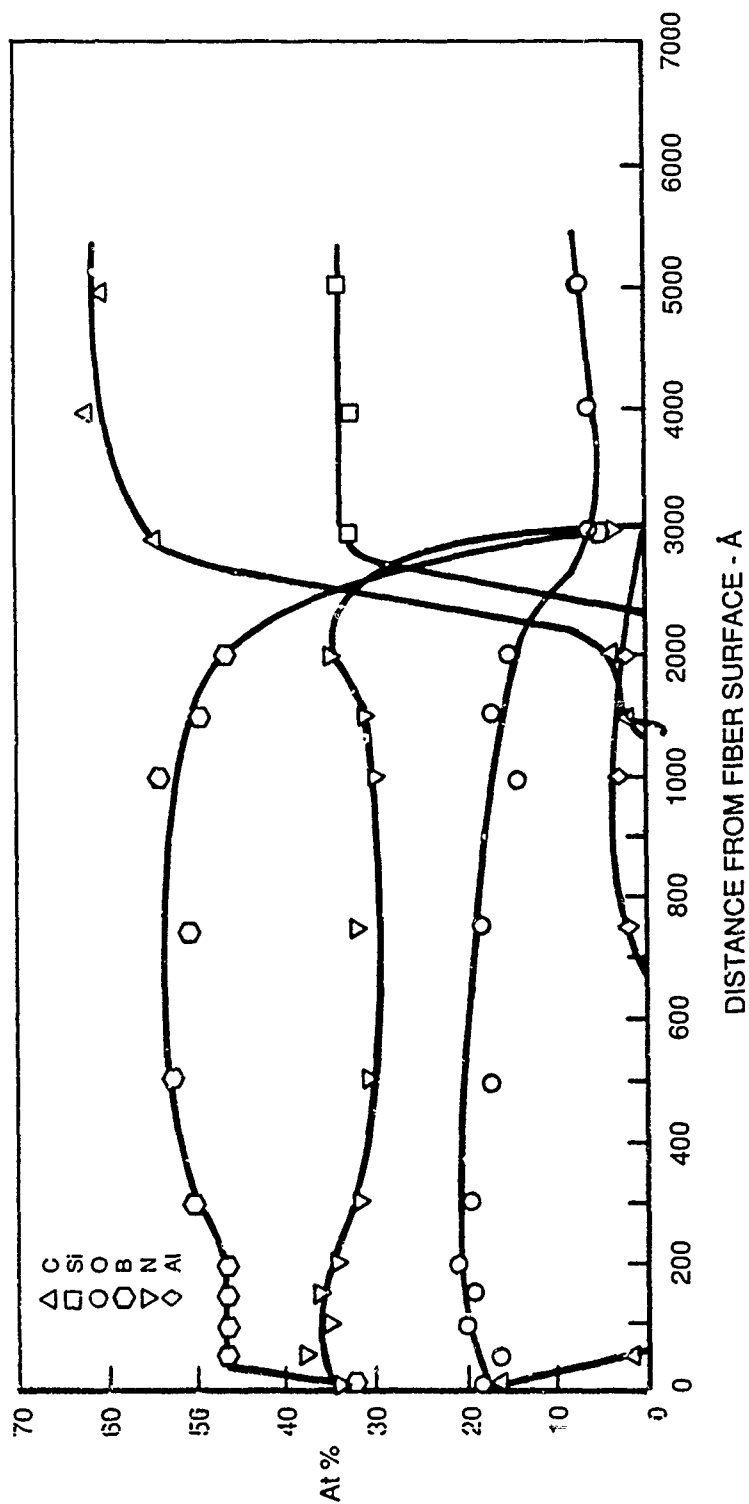
Fig. 32 SAM Depth Profile — Synterials BN Coated Nicalon Fiber, Lot #88-5-5
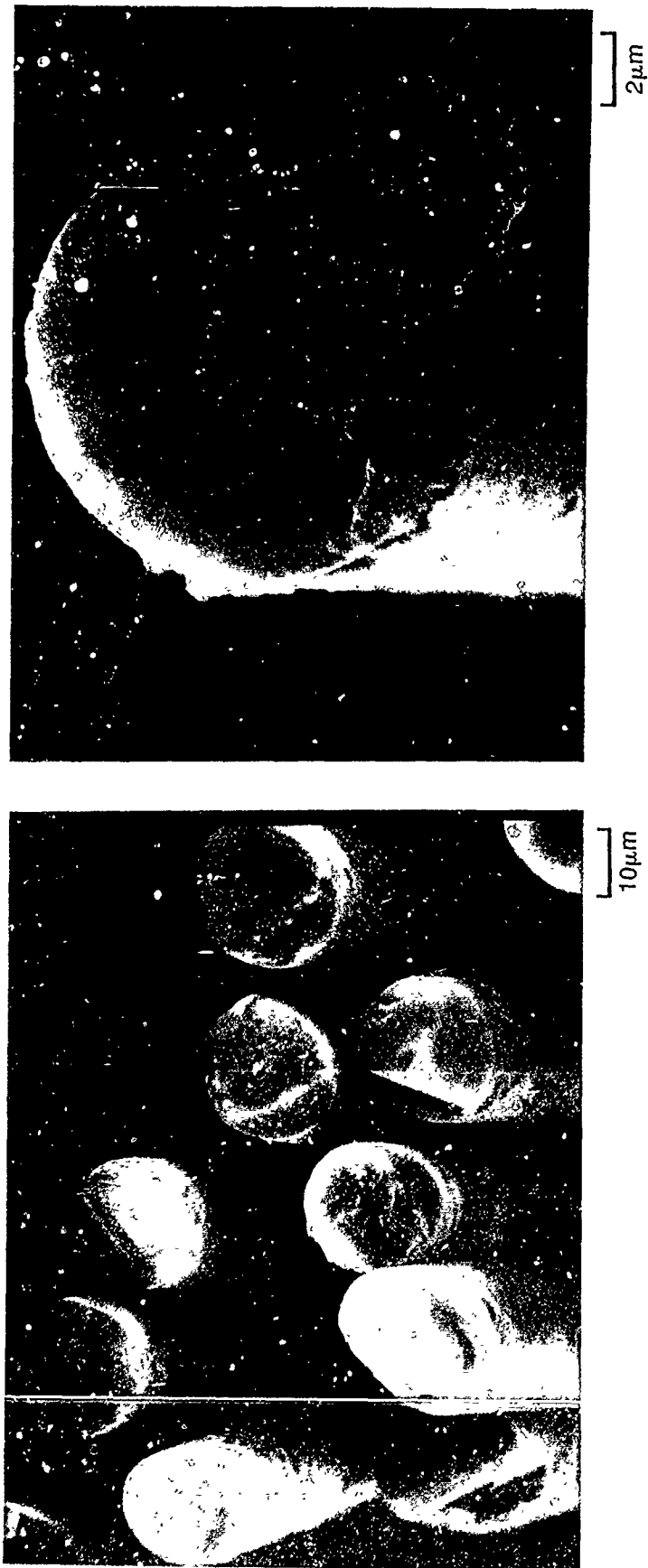
Fig. 33 SEM of General Atomics Sol-Gel Y_2O_3 Coated Nicalon Fibers [Lot #39066-127, UTS=202 ksi (1390 MPa)]
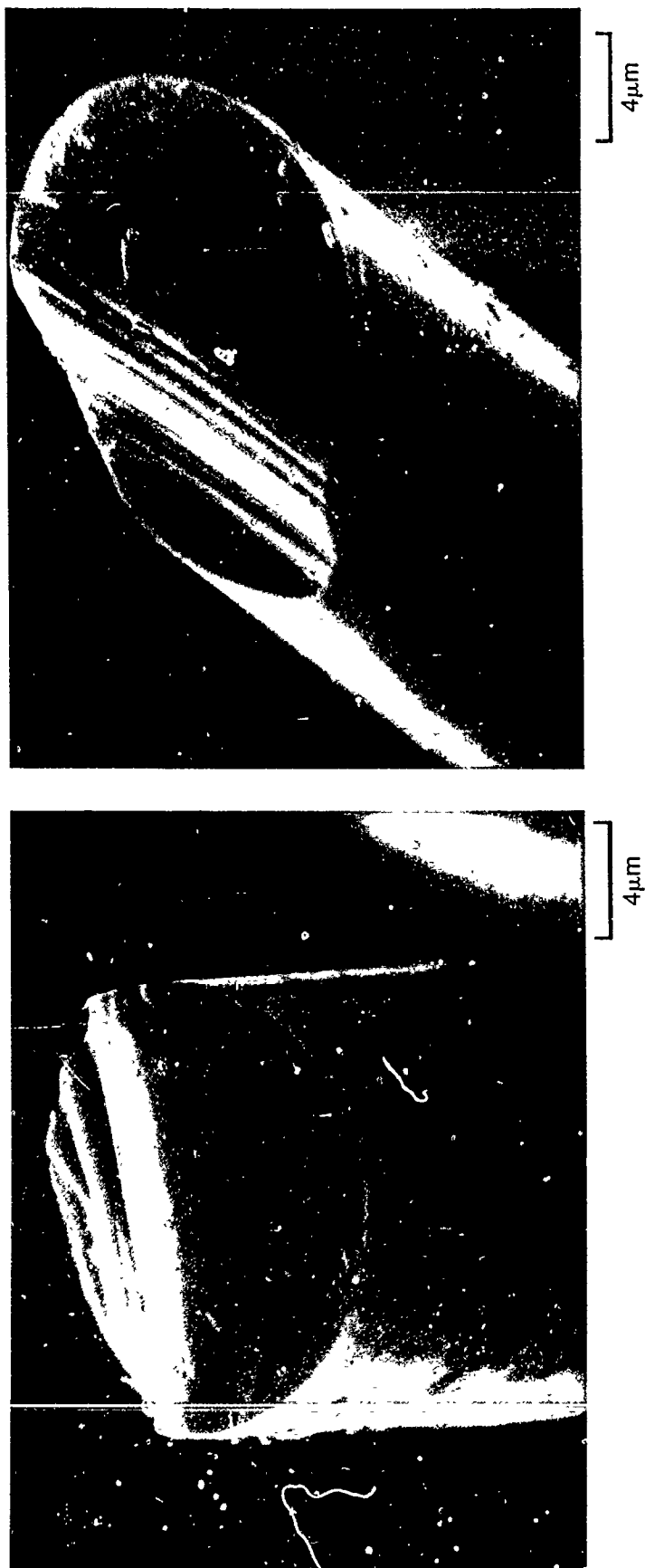
Fig. 34 Fracture Surfaces of As-Received G.A. Y₂O₃ Coated Nicalon Fibers (Lot YN-10399-7-3) UTS=267 ksi (1840 MPa)

90-6-16 '15
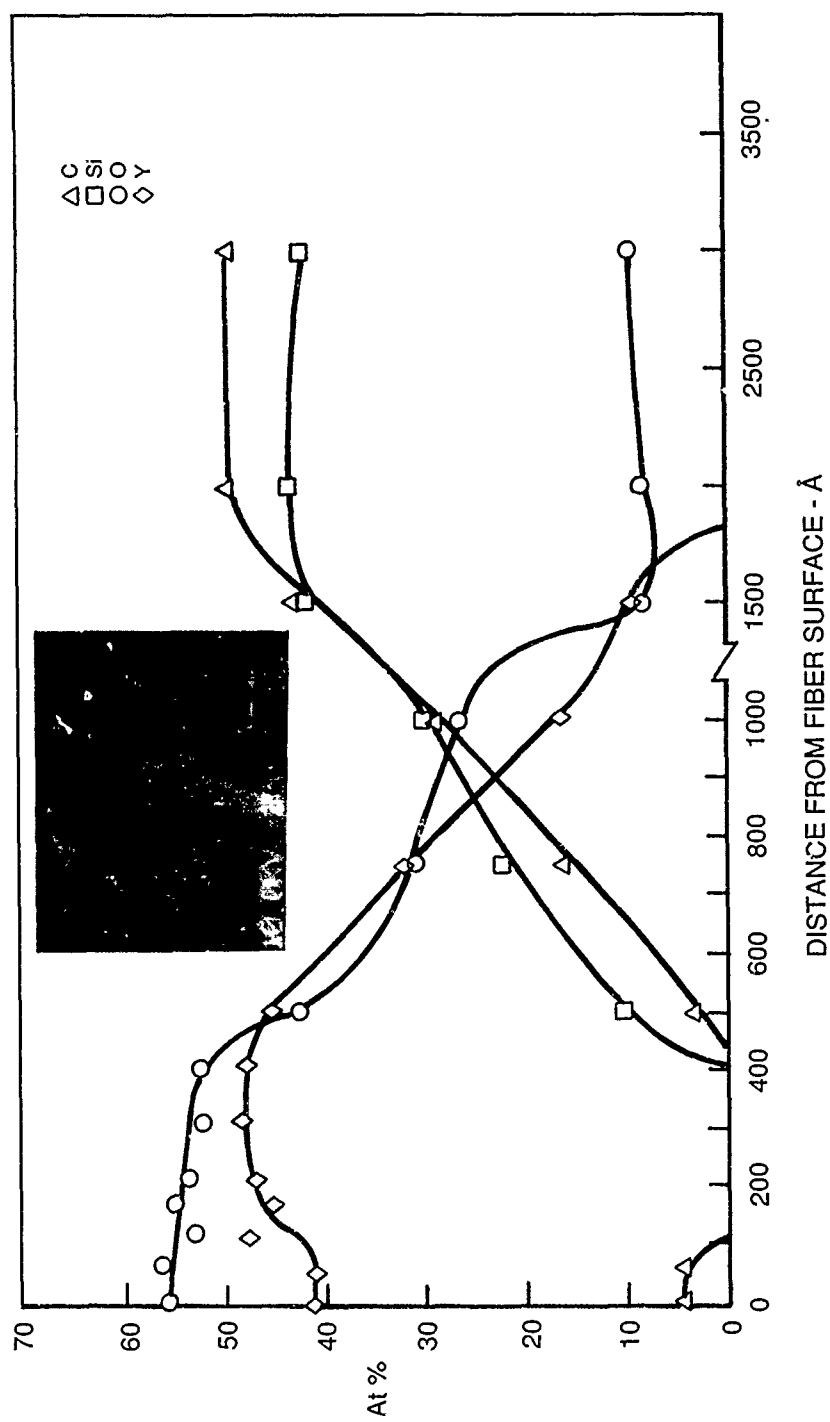
Fig. 35 SAM Depth Profile — General Atomics Y_2O_3 Coated Nicalon Fiber (Lot #39066-127)
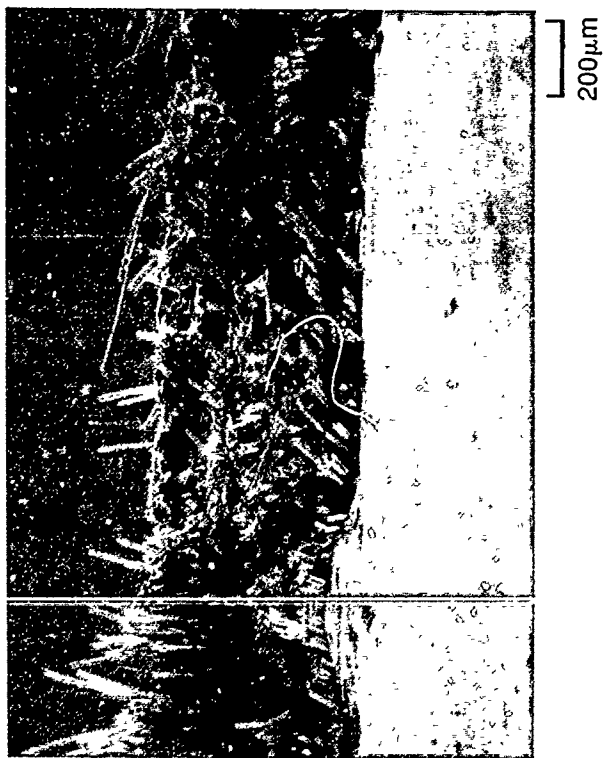
Fig. 36 Fracture Surface of LAS Matrix/G.A. Y_2O_3 Coated Nicalon Fiber Composite #51-90 [RT σ=89 ksi (614 MPa)]
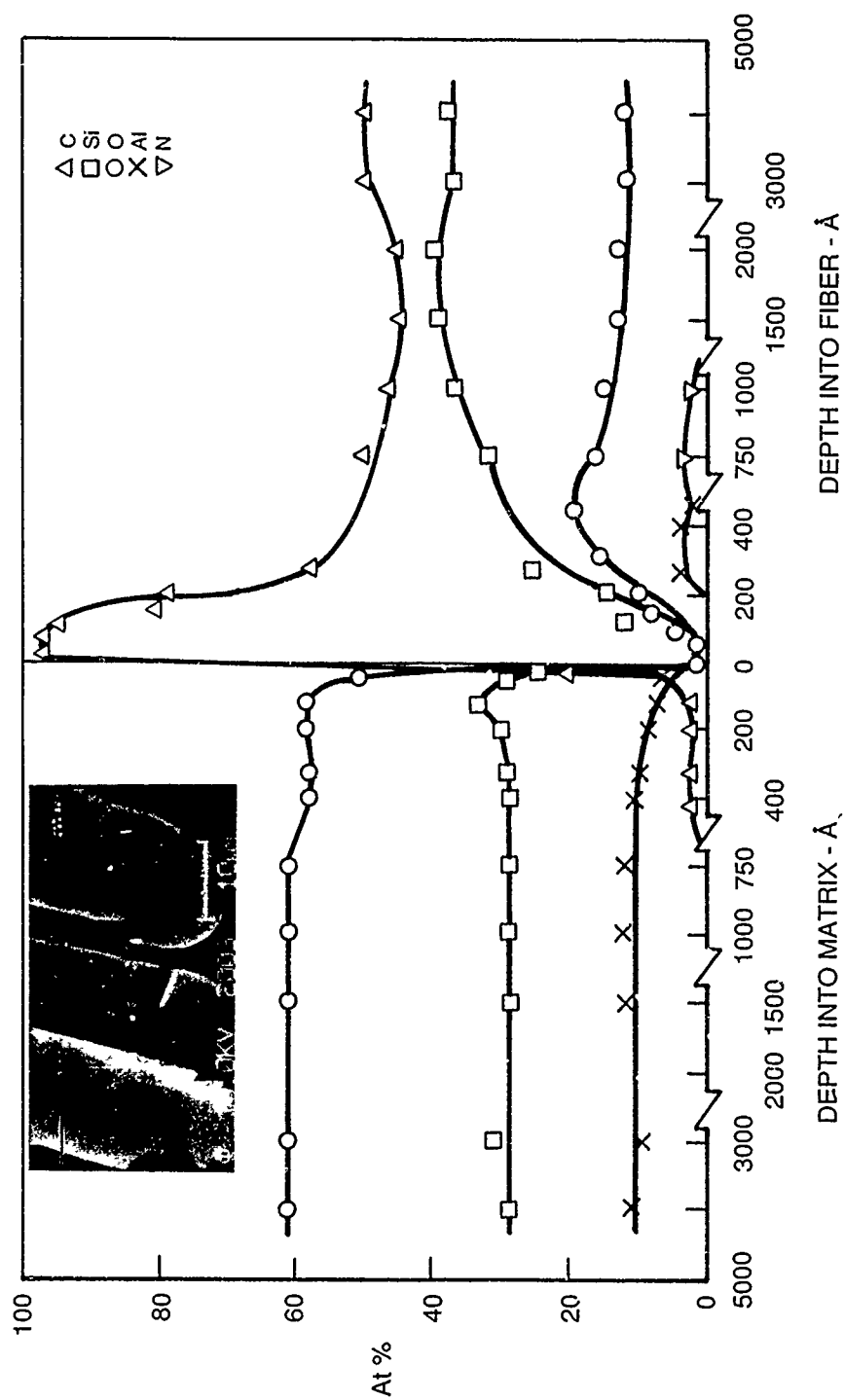
Fig. 37 SAM Depth Profile — Interfacial Chemistry of LAS Matrix/G.A. Y_2O_3 Coated Nicalon Fiber Composite #51-90

90-6-16-38
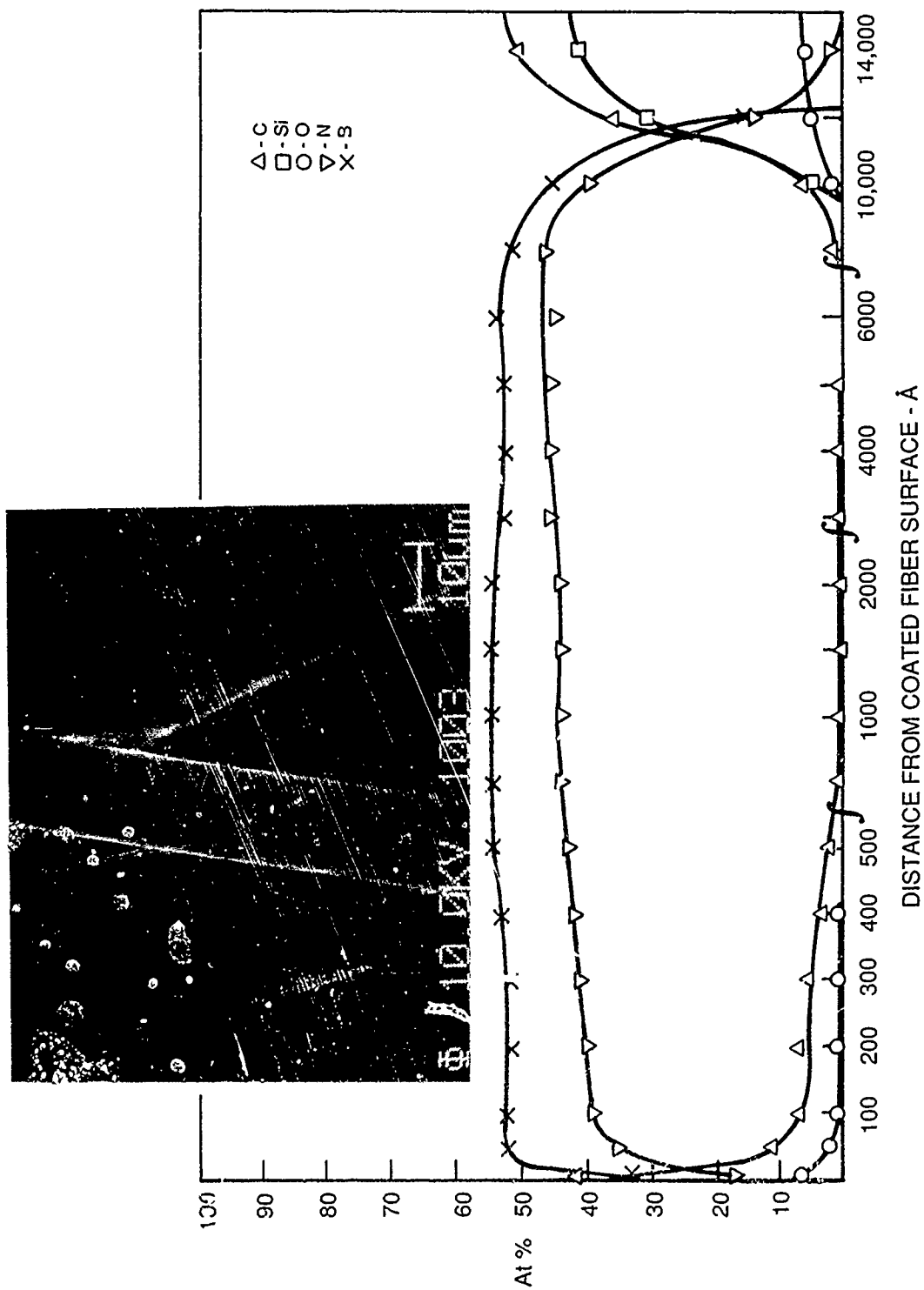
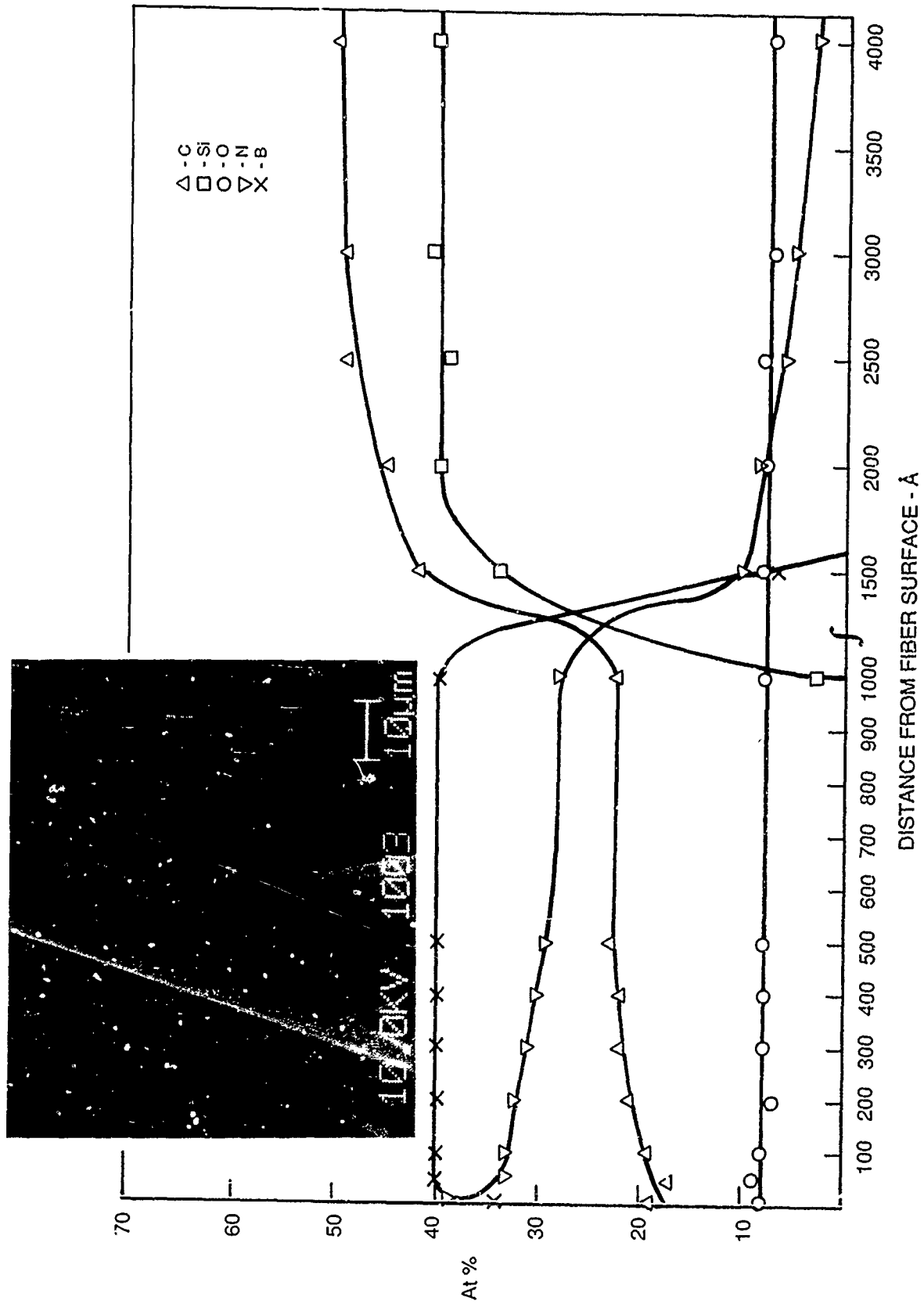Fig. 38 SAM Depth Profile — G.A. BN Coated Nicalon Fibers - Run #10193-74, 500°C, 30 min

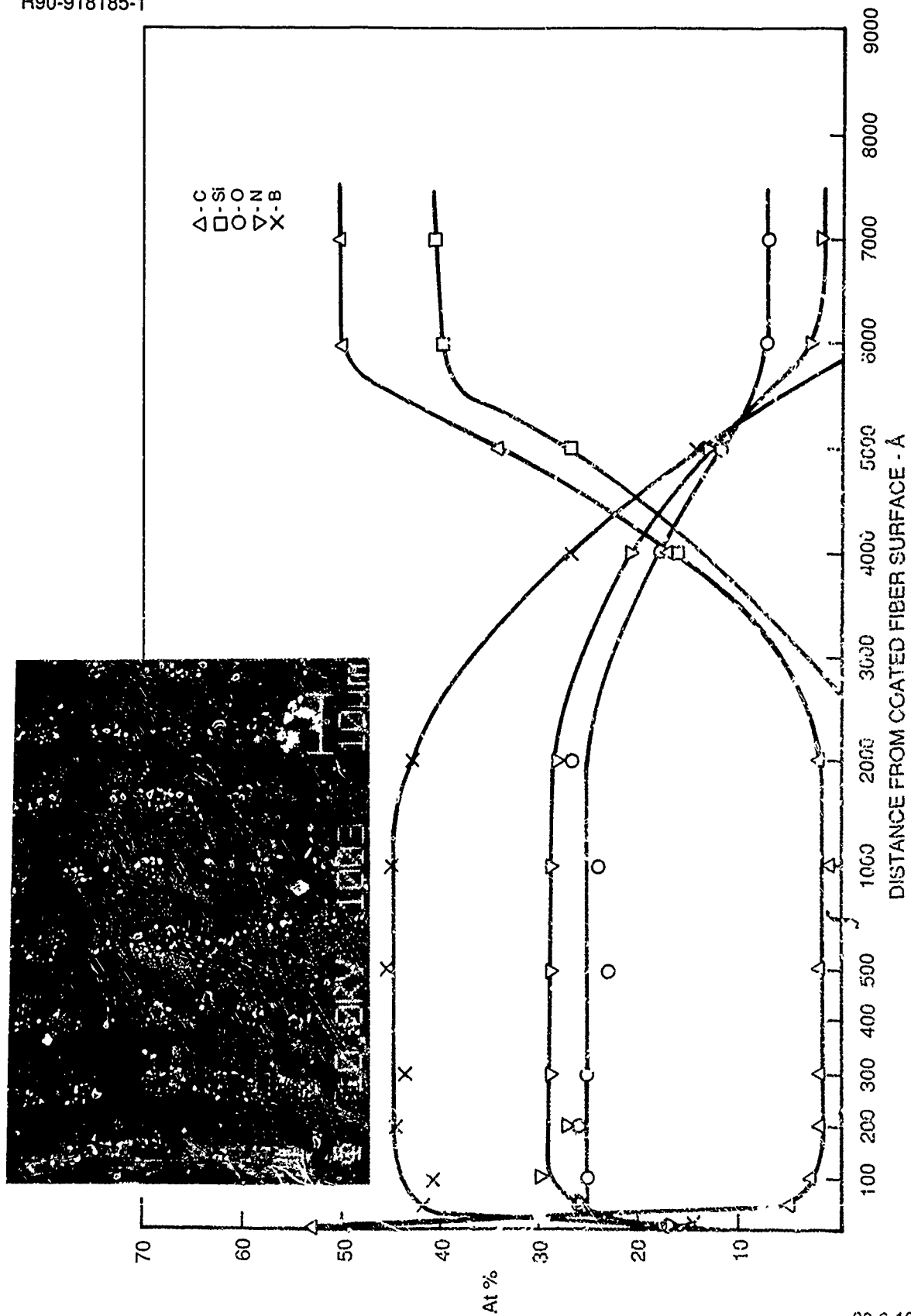Fig. 39 SAM Depth Profile — G.A. BN Coated Nicalon Fibers - Lot #10193-69, 800°C, 25 min

90-6-16-40

Fig. 49 SAM Depth Profile — G.A. BN Coated Nicalon Fibers - Run #10192-75, 800°C, 30 min (Smooth Fiber), RT UTS=272±72 ksi (1677±497 MPa)
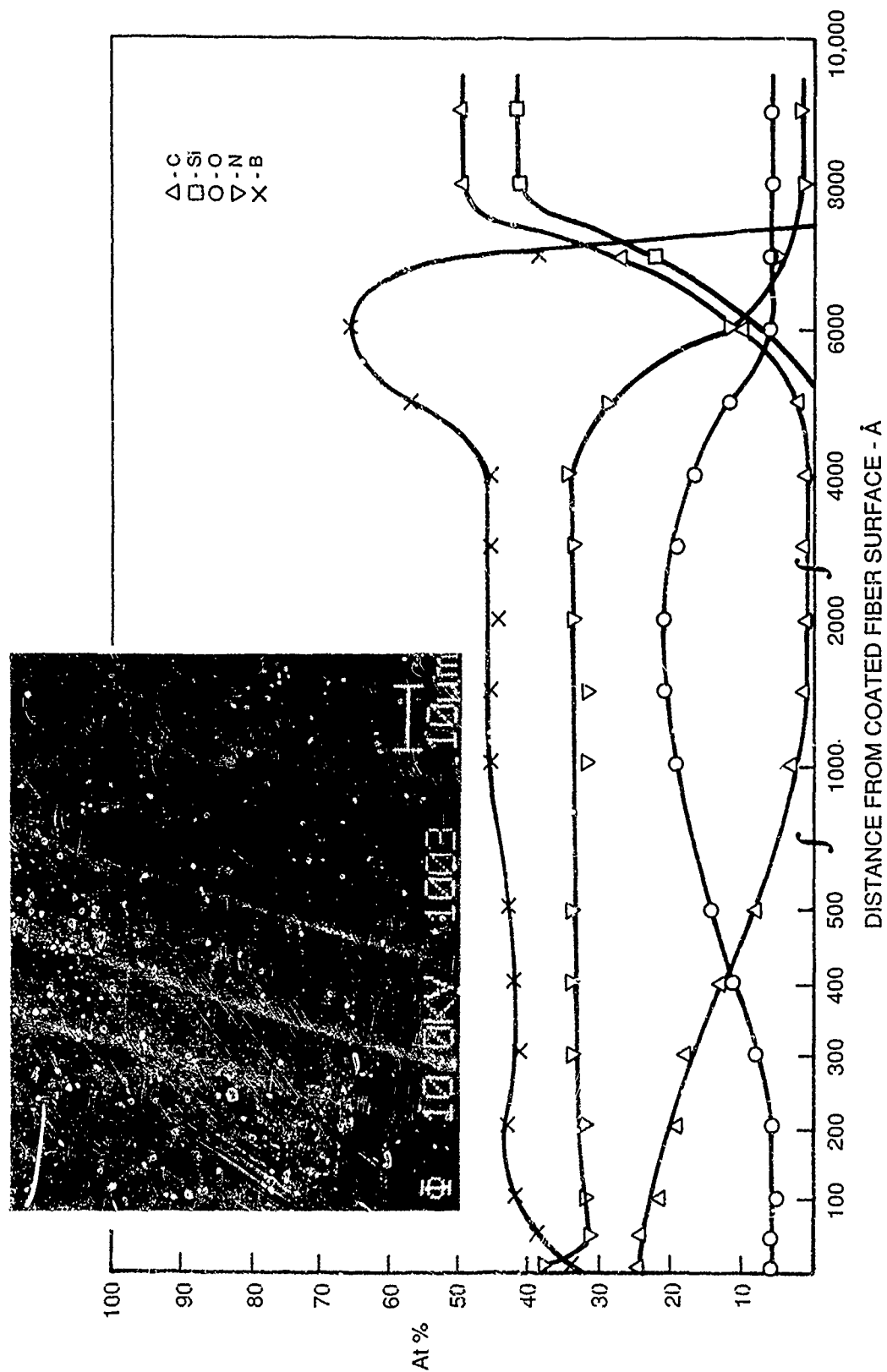
90-6-16-41

Fig. 41 SAM Depth Profile — G.A. BN Coated Nicalon Fibers - Run #10193-76, 1000°C, 30 min, RT UTS=263±65 ksi (1815±448 MPa)
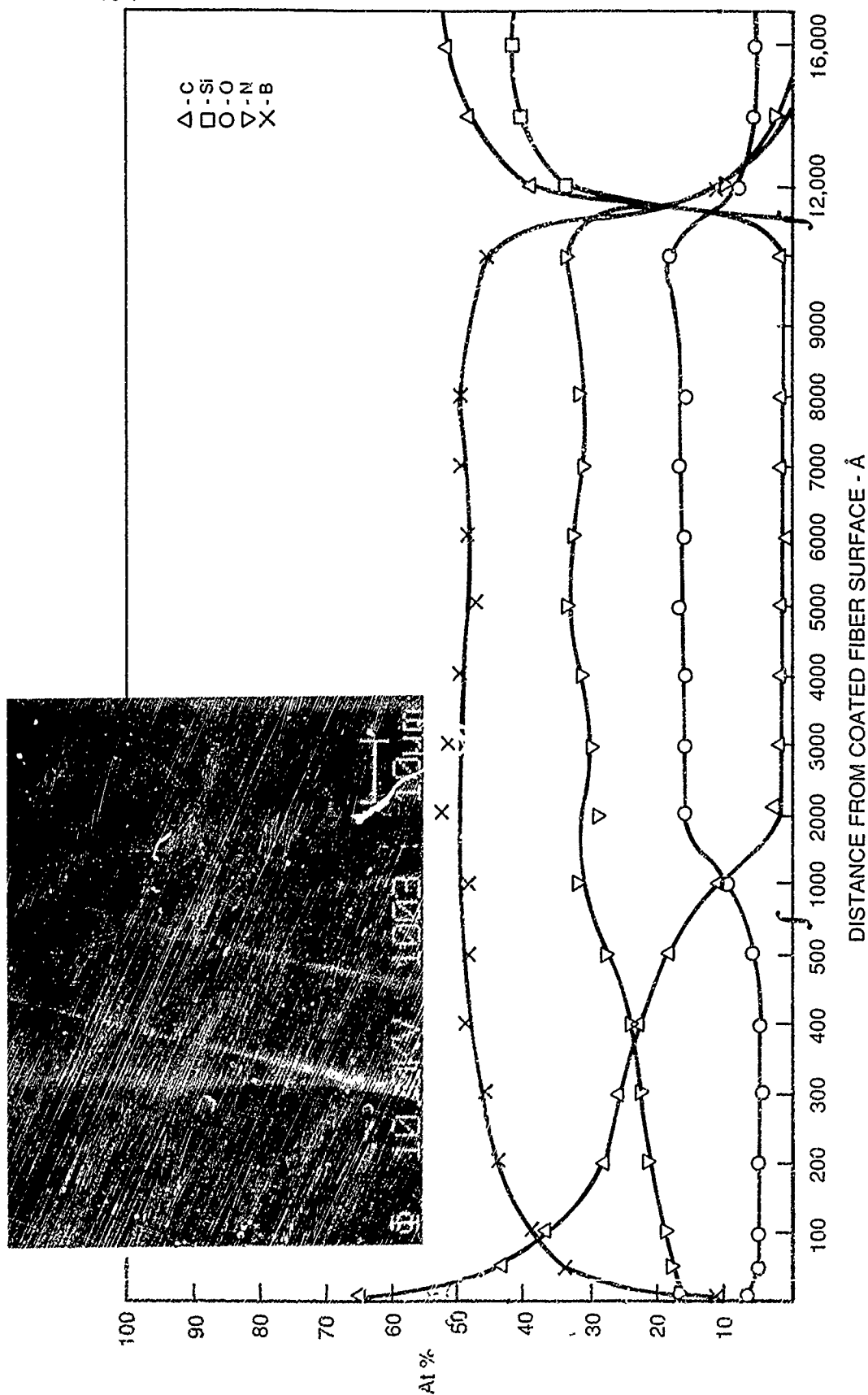
90-6-16-42

Fig. 42 SAM Depth Profile — G.A. BN Coated Nicalon Fibers - Run #10193-77, 1000°C, 65 min, RT UTS=262±64 ksi (1808±442 MPa)